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FOUNDATIONS AND METHODS
OF
CHEMICAL ANALYSIS
BY THE
EMISSION SPECTRUM

Being the Authorised Translation of
“*DIE CHEMISCHE EMISSIONSSPEKTRALANALYSE*”

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PREFACE

Throughout the last seven years, partly in collaboration with Dr. E. Schweitzer, the writer of this preface has been engaged upon the study of the problem of qualitative and quantitative analysis by means of emission spectra. The work has its inception in the study of certain special problems submitted by colleagues engaged in technical operations. These investigations encouraged a belief in the practicability of organizing a systematic study of the whole subject, and of devising absolute methods for the application of a quantitative system of spectrum analysis. Some of the practical procedures and technically significant examples have already appeared in a fairly extensive series of communications published in the "Zeitschrift für anorganische und allgemeine Chemie" and in the "Zeitschrift für Metallkunde" as well as in the "Metallwirtschaft."

At an early stage the attention with which these accounts met in the metal industry resulted in an avalanche of enquiries respecting details, and—which was still more significant—in prolonged visits from colleagues attached to industrial establishments, who wished to become practically acquainted with the methods which had been devised. Material for experimental research was rendered available in great wealth and variety by the courtesy and generous assistance of the Deutsche Gesellschaft für Metallkunde as well as numerous firms, notably the Deutsche Gold-und-Silber-Scheideanstalt, Heraeus (Hanau) Goldschmidt (Essen), Akkumulatorenfabrik Hagen, I.G. Griesheim (Elektron and Bitterfeld). Thanks to the valuable material placed so liberally at the authors' disposal, they have been enabled to accumulate a store of experiences which they have embodied in this book together with numerous hitherto unpublished experiments. Their chief aim was to establish the method on a firm physical basis by a systematic generalization of the special methods and problems which have come under investigation.

The underlying foundation of the investigations discussed in the book is furnished by our conception of the nature of the luminosity of the spectrum and the structure of the atoms, that is to say, by the modern physical analysis of the spectrum. As it is the physical study of the spectrum which shows the way in the search of means in the

service of the chemical application of spectrum analysis, so it is also our physical interpretation of spectrum analysis which indicates where the limits of chemical analysis with the aid of the spectrum are to be looked for. It points to the possible errors and the means whereby they may be eliminated.

As far as the practicability of the method, its trustworthiness, and the fundamental establishment of the method as such as well as its special procedures are concerned, the authors believe they have reached a certain measure of finality. They feel likewise assured that its practical applications will prove capable of adaptation to special purposes. Efforts in this direction, however, go beyond the boundary which the authors have set themselves in this their initial investigation of the problem. They propose to confine themselves in their work almost entirely to their own experiments. They have not attempted to treat the subject from different aspects, comprehensive accounts of which are not wanting. On the other hand, all that the authors regard as in the nature of fresh contributions to the solution of older problems has been treated in considerable detail. Similarly, references to other publications are restricted to those which have a direct bearing upon the authors' experiments. This applies alike to old and new work. A short appendix only gives references to other particularly significant papers. The book does not in any way concern itself with analyses based upon the fluorescent and phosphorescent properties of substances, the application of the discharges of gases in vacuum tubes, analyses by absorption spectra, and quantitative analysis by X-rays and electron impact.

It is hoped that the matter brought forward in this book may serve to show that analysis by the emission spectrum provides new methods of investigation in connection with technical processes, and admits of problems concerning metals being dealt with such as hitherto could not be brought within the scope of scientific control. Incidentally the development of chemical analysis by the emission spectrum supplies yet another instance of the great service which pure physical research, experimental as well as theoretical, is capable of rendering by its direct application to the practical solution of modern technical problems.

This book reached completion during the period of the writer's transference from Tübingen to Munich. On such occasions when life enters upon a new phase an investigator may be forgiven for allowing his thoughts to swerve from the matter in hand and to dwell for a moment upon personal impressions and recollections of the preceding phase, especially where these thoughts are intimately connected with the work recorded in such a book as this. The writer experiences an urgent need to conclude these introductory remarks by giving expres-

sion to his sense of gratitude to Dr. C. Bauer, of the Ministry of Education of the State of Württemberg, to whom he is indebted for an incomparable wealth of resources, for a never failing readiness to afford moral and material support, and for his generous attitude to the authors' aim and work throughout the five years during which the work was proceeding at Tübingen.

W. GERLACH.

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CHAPTER I

NATURE AND APPLICATION OF CHEMICAL SPECTRUM ANALYSIS

Chemical spectrum analysis, in whatever way it may be applied, is based upon the investigations of Robert W. Bunsen and Gustav Kirchhoff, who showed that the chemical composition of a vapour may be recognized by its emission or absorption spectrum. Where the spectrum exhibits lines it is to be concluded that atoms are present in the vapour. Where it is composed of bands the inference is that the vapour contains molecules. This distinction in itself constitutes a chemical analysis of the simplest kind, though for experimental reasons it is not easily capable of general application. Nevertheless, as an analytical principle it is more significant than was conceded until lately. Thus, the absorption spectrum readily proves that the vapour of bismuth or antimony contains a considerable proportion of molecules, whereas it is an exceedingly elaborate process to do so by vapour density tests. Not only that : the occurrence of banded absorption in the vapours of metals which hitherto were universally regarded as uni-molecular, like those of the alkalis, zinc, cadmium, mercury, lead, has disclosed the existence of molecules of mercury and associated rare gas molecules and many other unexpected, unknown, and curious anomalies, and thus has attained the utmost significance in the elucidation of the highly interesting modern problem of the chemical formation of molecules. Molecules which are formed or undergo changes under the influence of electrical discharges cannot in many cases be detected by chemical means owing to their instability, whereas their presence may readily be demonstrated by observing the simultaneously occurring emission or absorption of the reacting vapour. In this category we must include the group of problems relating to the optical determination of chemical heat of reaction, in which very considerable advance has been made of late by J. Franck and his school, as well as Victor Henri's spectroscopic investigations of the behaviour of gaseous reactions.

These, however, are not questions which concern us here. The problem with which we have to deal is the most primary and simplest of all that may arise. It embraces solely, as a means of establishing a practical mode of analysis, the *identification and quantitative deter-*

mination of an element occurring in more or less pronounced proportions in another element. It is a problem upon which many contributors have worked, among these being Hartley, de Gramont, Leonard and Pollok, but the practicable solution of which in general and in its quantitative aspects in particular has again and again been questioned.

The foundation upon which *qualitative* analysis by the emission spectrum rests is the fact that an element which has been rendered luminous emits certain invariable spectrum-lines which are characteristic of it. The *quantitative* aspect of spectrum analysis has its inception in the fact that these characteristic spectrum-lines differ in their intensity and it rests upon the two suppositions that, other things being equal, the intensity of a spectrum-line is governed by the number of the luminous atoms in the source of light, and that the number of the luminous atoms is proportional to the aggregate number of the atoms of a like kind. Further, it is assumed that a mixture of two elements, when rendered luminous, sends forth the spectrum-lines of both elements.

And yet this last supposition, obvious though it may seem, is not maintainable in fact. We proceed to demonstrate this in view of another mode of application of spectrum analysis which in the course of recent decades had completely thrust into the background the chemical side of spectrum analysis, and perhaps we might add that it was a fortunate thing that this happened. We are referring to the use of spectrum-lines as a means of enlarging our conception of the *structure of the atoms*. Indeed the practicability of a well-founded chemical system of spectrum analysis has only been brought about by taking full cognizance of the physical nature and the structure of the spectra as well as the physical conditions which determine the emission of certain lines of the spectrum and the non-appearance of others.

We shall proceed from a very simple example, viz. the spectrum of atmospheric nitrogen. If this be rendered luminous, say by the passage of a current through a vacuum-tube, what will be seen at the outset will be the spectrum of pure nitrogen, this being the spectrum of the nitrogen molecule; in other words, we see bands.¹

¹ Every spectrum of the molecule consists of groups of numerous lines. The energy of vibration arising from the excitation of the electrons, the so-called "electron jump" which is the source of the emission of a spectrum-line, has superimposed upon it the energies of the vibrations which the atoms of the molecule may execute in the molecule relatively to one another and about one another. This may be regarded as the first achievement of the physical investigation of the luminosity of the spectrum, which in our days has led to the analysis of the structure of the molecule. It has so far not been attempted to investigate the practicability of applying band spectra for the purposes of quantitative analysis, and investigation in this direction is likely to present great difficulties. Even for the purposes of qualitative chemical analysis they often can only be used with great difficulty owing to their complicated character and the similarity of the spectra of related molecules.

It is not difficult to so choose the electrical conditions obtaining in the working of the vacuum tube that the line-spectrum of the nitrogen atom may likewise appear, the necessary condition being that the nitrogen molecules should be dissociated into atoms and the latter thereupon rendered luminous.

This in itself teaches us something respecting chemical spectrum analysis. It shows that if we wish to recognize an element from the properties of its line-spectrum, the conditions under which the luminosity is excited should be such as to bring about the dissociation of chemical combinations.

Now, atmospheric nitrogen contains also the *rare gases* of the air (which as such occur therein in an atomic gaseous state).

Although 1.2 per cent. of argon is present, the spectro-analytical method fails in any attempt to demonstrate its presence. It fails even in concentrations millions of times greater than those in which sodium, to give an instance, imparts a distinctly yellow colour to the Bunsen flame. If a vacuum-tube be filled with rare gases, say with helium and argon in equal proportions, the argon alone will be found to acquire luminosity, and in order to obtain the entire spectrum of helium it becomes necessary to employ extremely pure helium.

Applied to chemical spectrum analysis these experiments indicate that even the presence of an element in the atomic state may not suffice to render the element identifiable in its spectrum. *The conditions of excitation, in fact, require to be such that the element which is to be identified may likewise become luminous.*

The energy of excitation of a spectrum-line of the atom is as characteristic for the latter as the wavelength of its spectrum lines. Bohr's quantum theory of the atom accounts for this fact, in that the energy of excitation E is transformed into monochromatic energy of radiation in accordance with the quantum frequency relation $E = h\nu$ (where h is Planck's constant, and ν the frequency of the spectrum-line). Each frequency, *i.e.* each spectrum-line, has accordingly a characteristic energy of excitation belonging to it.

The systematic investigations of these questions of excitation have supplied the foundations of an important section of modern astrophysical research and have provided the means by which it becomes practicable from the occurrence of certain lines of an element in its spectrum, not merely to secure evidence of its "chemical" presence on a star, but to read off the physical conditions which necessarily obtain on the star in order that these lines may be emitted; in other words, they have established the basis of the chemical and physical analysis of the stars.

Fortunately, in the chemical spectrum analysis of metals the

conditions are in general simpler than those arising in the instance of a case relating to the identification of the rare gases. The conditions of excitation of different metals, if we except the alkalis, differ quantitatively only very little from one another, so that the spectrum of a mixture (alloy or compound) of metals will generally exhibit the whole of the components.

The question now arises, whether the presence of an element in a source of light exercises an influence upon the emission of another element in some such way that the intensity of the spectrum-lines is affected by the nature of the elements which happen to be present. In the realm of physics a number of such influences are known, all of which are fundamentally possible. They all arise from the fact that an atom subjected to excitation, instead of radiating its energy, may transfer it by impact to another atom, in which case it will be the latter which radiates. The authors, while they do not contest their feasibility, have not discovered such mutual influences. Their probability does not, however, appear to be more than remote since the collisions between the atoms of the metals are rarer than in the molecules of the atmospheric gases.

Greater importance, however, attaches to another phenomenon. Observation shows that the intensity of the spectrum-lines of an element, when induced by sparks from liquids, is *very greatly* affected by alkali salts which may be present (or which may have been added for the purpose of increasing the conductivity), and, similarly, by the anion of the salt. These effects are doubtless due to the variation in the discharge and the pronounced share which the primary salt or the added salt takes in the conduction of the current. They introduce difficulties in any absolute quantitative analysis, whether a fluid spark-gap or an arc are formed between carbons impregnated with a salt be employed. In the method here described they were, however, never found to interfere noticeably with the course of the experiment (see pp. 83 *et seq.*)

In this connection a fresh element of doubt presents itself. This arises when the spectrum of a metal is to be excited by the discharge of an electric spark between two electrodes consisting of the metal in question, that is to say, by impressing a high tension upon the electrodes. As the spark leaps over, minute chips of the metal are liable to be detached and to volatilize in the spark-gap (the temperatures being there of the order of 5000 to 10000° C.).

The electrodes are heated within the very small spark-gap by the impact of ions and electrons and likewise volatilize. The spectrum is in the major part a line-spectrum, in which, however, there are also bands of the molecules of the atmospheric gases or of compounds of the metallic vapour with the air-gases. We shall disregard these bands,

and, in order to render this practicable, the conditions under which the electric spark is generated shall be so chosen as to minimize the occurrence of bands liable to mask the line-spectrum and render it difficult to decipher it.

It is found that the line-spectrum of a pure metal presents a widely variable appearance when the electrical conditions of the spark are varied, such as the rate of spark discharges per second, the electric voltage, the conditions under which the spark passes across the gap, which result, for example, from variations in the magnitude of the capacity and self-induction of the spark circuit. Thus, the higher the voltage and the energy chosen, the more intense will be certain lines of the spectrum, while others lose in intensity. There is a physical explanation to this also. The vapour of a spark invariably contains a mixture of atoms and ions of the metal, and each has its own peculiar spectrum. As the energy rises, so also does the number of ions and the intensity of the ionic spectrum in relation to the atomic spectrum.¹ Since the latter is particularly intense when it emanates from the electric arc under a low voltage, while the former is chiefly obtained under a high voltage in the spark-gap, the two spectra are frequently referred to as *arc* and *spark spectra* respectively. The arc-spectrum is accordingly the spectrum of the neutral atom, while the spark-spectrum is the spectrum of the ion. Recently another mode of distinguishing these two spectra has become current. The spectrum of the neutral atom of a metal *Me* is denoted by the symbol *Me I*, while that of the simple, double etc. positive ion is referred to by the notations *Me II*, *Me III*, etc. It must not, however, be supposed that the arc contains no spark-lines, and that there are no arc-lines in the spark-spectrum. In any source of light in which there is luminous metallic vapour, thus even in the simple Bunsen flame, there is invariably a mixture of neutral atoms and positive ions of the metal. The ratio of mixture is essentially a matter of the temperature of the source of light and the work of ionization of the metallic atoms. Since the passage of the discharge in a spark is greatly influenced by the density of the vapour, the ratio of the intensities of the arc-lines and those of the spark-lines is likewise governed by the amount of the vapour, which in its turn is dependent upon the energy (temperature) and likewise upon the vapour pressure of the electrode metal.

The physical aspect of spectrum analysis has demonstrated that the spectrum of the atom, like that of the ion, is made up of various series. Without attempting to discuss the significance of these regular

¹ The magnitude of the energy of ionisation is characteristic for each atom. For all atoms of metals it is much of the same order of magnitude (viz. 3 volts for caesium up to 10 volts for mercury).

sequences of spectrum-lines, we may characterize the various series as the spectra of the "stages of excitation" or "states of excitation" of an atom, and picture to ourselves these "stages of excitation" as the stages of transition from the atom to the first ion, from the first ion to the second, and so forth. Since the conditions under which the excitation from stage to stage (frequently denoted by *Me I'*, *Me I''*, or *Me II'*, *Me II''*, etc.) are likewise dependent upon the energy in the source of light, it follows that apart from the ratio of mixture *Me I*, *Me II*, etc., the ratios of mixture *Me I'*, *Me I''*, etc. likewise exercise a determining influence upon the intensity of the spectrum-lines. Very little is known as yet regarding the interdependence of the intensity of the various series of spectra and the excitation of the electrical discharge, to mention an example. It is therefore not surprising that the hesitation which is felt in accepting a system of chemical analysis which rests upon the intensity of the spectrum-lines should arise primarily out of this gap in our knowledge. We shall see later (pp. 67 and 68) how these objections may be overcome, and how the spectrum itself is made to furnish an indication of the presence or absence of the "normal" conditions of excitation in the process of its production.

Where each electrode contains a mixture of two metals qualitative chemical analysis can be achieved with comparative ease. Their presence may then be readily ascertained from tabulated values of the arc and spark lines of the metals.

Nor is it difficult to recognize the feasibility of a method of *relative quantitative analysis*. If in a mixture of two kinds of atoms, one proceeds to continuously diminish one of the components, its spectrum-lines become fainter and fainter. The initially faint lines will vanish first, and ultimately the initially strong spectrum-lines will follow suit. These are briefly referred to as "ultimate lines" (also persistent lines, residuary lines, *raies ultimes*) or "sensitive¹ lines" ("raies sensibles") in that they enable one to detect the slightest traces of an element.

Quantitative analysis, however, being constrained to rely upon the intensity of the spectrum-lines of the elements would not seem to be feasible, since, as we have already noted, the intensity depends for different spectrum-lines in entirely different ways upon the energy, the electrical conditions of the spark, the vapour pressure, and so forth. A mode of *chemical analysis* is accordingly conceivable only if all analyses are invariably carried out under identical electrical conditions.

We shall show later that it is precisely by reason of the interdependence between the numerical relation of atoms to ions in the spark vapour and

¹ The notion of the "sensitivity" of a spectrum line of an atom in connection with chemical analysis is explained in Chapter II, a—c.

the conditions of discharge that the spark-spectrum admits of the reproduction of these conditions.

We now proceed to give in condensed form a conspectus of the analytical problems which come within the scope of chemical spectrum analysis. Most of them will be discussed in their fundamental or special bearings.

In this summary we shall more particularly deal with four prominent aspects of the method of spectrum analysis whereby it surpasses the practical resources of chemical analysis. These four are *expedition*, the possibility of analysis of *minute quantities of material*, the entire *preservation of the available material*, and the facility of *ascertaining the distribution of an element in a given substance*. It will be shown that the whole of the advantages obtainable by the spectrographic method of analysis are rendered available in their widest scope by the use of spark-spectra.

We will not omit to give it as our opinion that the method of quantitative spectrum analysis should by no means be regarded as a competitor of the chemical method, and it cannot indeed take its place where the composition of a substance is to be determined with the utmost quantitative precision. Such a chemical analysis aiming at a degree of scientific exactness implies that two conditions may be fulfilled. A sufficient amount of the substance in question must be available and in many cases the analyst must not be pressed for time. Both in industrial and scientific investigations a very large range of problems presents itself where these very conditions cannot be fulfilled. Moreover, it may happen that a specimen contains metals in small or even minute quantities, in which case chemical analysis is not practicable.

Respecting the *rapidity of the spectro-analytical method* the following points may be noted: Where a complete qualitative analysis of a specimen of metal is required it is generally sufficient to take several spectrograms upon one plate in succession. This, including the development of the plate, can be accomplished in about 20 minutes. The evaluation of the spectrograms at once discloses all the metals present in considerable proportions, say above 0.1 per cent., to one knowing his spectrum apparatus. In doubtful cases it may be necessary to measure the position of suspected lines relatively to known lines with the aid of some apparatus designed for the determination of spectrum-lines (such as the Zeiss Abbe comparator, the Zeiss photographic plate measuring microscope, or similar instruments by Fuess, Hilger, Askania Works, etc.) These measurements of the wavelengths and the identification of the elements derived therefrom, excepting in abnormal cases, occupy an hour at the outside. The qualitative analysis of all the

metals present, which will be treated in detail in Chapter IV., usually includes some special aim. It may, for instance, be required to ascertain whether a certain element A is present in the sample, or whether the proportion of A is above or below a certain concentration. This "absolute" analysis and the incidental "limiting concentration" may be directly read from a single spectrogram. The limits of the admissible concentration or of the maximum concentration which an impurity in a metal or a component of an alloy may not exceed can be ascertained with particular expedition and reliable precision by means of the spectro-analytical method. Since in many instances the presence of exceedingly minute impurities exercises a marked influence upon the qualities of a metal, notably upon its mechanical properties, laborious mechanical tests and checks may be avoided by the application of the spectro-analytical investigation. In many cases the spectrum analysis may even indicate the *raison d'être* of the deleterious effects of the presence of minute impurities or additions: (see, for instance, the observations on the grain boundary effect, Chap VII, b).

The requisite amounts of material are extraordinarily small. Pieces a few millimetres long often suffice by way of electrodes. The authors have even been able to apply the analysis to individual granules occurring as enclosures in a metal and extracted by mechanical preparation, though these fragments were no larger than a very small pin's head. Small pieces of this kind may be subjected to analysis by such means as embedding them by pressure in the end of an electrode of pure calcium, or, still better, of gold, or by attaching them by fusion (see p. 39, fig. 9). Even powders may be examined by embedding them in a pure metal or small quantities of precipitates on a filter in accordance with the method described on p. 39, fig. 10.

The fact, however, that a *minute quantity* of material volatilizes during the taking of a spectrogram may be of considerable importance since this affords a means of testing the homogeneity or stratified composition of a specimen, which may be accomplished by successive series of spectrograms, the first of which discloses the composition of the surface layer, while the succeeding series furnish the analyses of layers of increasing depth; or the test may be applied by exposing different portions of a specimen to the impact of the spark. Particulars respecting these procedures will be found in Chap. VII on local analysis. In special cases the spectro-analytical method will thus be seen to be capable of disclosing not only the *nature and proportion of an added substance*, but also its *metallographic distribution*, as explained under the heading of "grain boundary tests" on p. 114, and all this may be accomplished by the use of extremely small quantities of material.

The spectro-analytical method may likewise be applied with success

as a means of differentiating *principal impurities* and *accidental impurities* (in this connection see also what is said regarding external and internal impurities in the chapter on "Qualitative Analysis" on p. 63), whereas chemical analyses not only prove abortive, but furnish entirely false data. Thus in one case chemical analysis had shown a light metal to contain a considerable proportion of copper. The analysis by the spectrographic method disclosed no copper content whatever. Obviously the chemically analyzed piece of metal had by some accidental link in the analytical chain become associated with an appreciable proportion of copper, in consequence of which the chemical analysis disclosed the presence of a mean copper content of n%.

In the majority of these experiments the excitation by the electrical spark is preferable to other methods of producing the spectrum, not only by reason of its simplicity, but also as it affords the *possibility of leaving intact the specimen which is to be analyzed*. Finished metallic objects may thus be analyzed, in that the slight ensuing roughening of the surface at the point where the spark is applied may readily be effaced.

Naturally cases arise where the spectro-analytical method may fail, viz. where so many elements are present that the very faint and few spectrum-lines of an ingredient present in minute proportion are too close to strong spectrum-lines of the other elements to be distinguishable in the spectrum.¹ In these cases the desired information will, however, be attainable by the combination of chemical separation and the spectrographic analysis of the separated components. In such cases, however, the available specimen cannot be maintained intact.

Neither may it be said that the spark excitation with solid electrodes is the only useful or practicable method of luminous excitation. In the first place, it is to be noted that even the spectrographic examination of solutions is practicable by the same method. In this case likewise very small quantities of dilute solutions suffice to make the analysis. Next, circumstances may arise where the analysis can be carried out to greater advantage when the solution is employed in the place of the solid electrode. For this class of analyses use may be made of the spark from liquid electrodes described in Chap. III. Finally, cases may arise where it becomes necessary to employ in the place of the method of spark excitation that of arc discharge, in which case small quantities (of the order of milligrammes) of the substance which is to be tested are volatilized in a carbon arc. From the investigations carried out so far it would also seem that for the demonstration

¹ In itself the analysis is capable of a practical solution with the aid of spectrum apparatus of maximum dispersion, but the complicated nature of the apparatus renders such a procedure useless for all practical purposes.

of the presence of such elements as arsenic, sulphur, selenium and tellurium, the method of spark excitation with solid electrodes is inferior in its performance to that of the solution spark and the arc discharge. The latter is probably likewise entitled to preference in the analysis of ores and minerals, especially as in these cases the preservation of a small specimen does not enter into consideration. In conclusion, we should not overlook the practicability of spraying solutions into the Bunsen flame. This method of producing a spectrum greatly restricts its range owing to the presence of very pronounced emission bands.

Before proceeding to discuss the special methods referred to, we propose to give an account of the investigations carried out by us on the fundamental practicability and the first principles of spectrographic analysis.

CHAPTER II

THE FOUNDATIONS OF CHEMICAL SPECTRUM ANALYSIS :
ANALYTICAL SENSITIVITY AND THE PRACTICABILITY OF
DETECTING A SPECTRUM-LINE

(a) ABSOLUTE SENSITIVITY AND "ULTIMATE LINES"

It is beyond doubt that in the sense in which the term is used by de Gramont the "ultimate lines" constitute the basic lines of the spectrum of an element. It is, however, an entirely different question as to whether these "ultimate lines" are also the *most sensitive* lines for the identification of an element and therefore those *best adapted* for chemical analysis by the spectrum. The answer to this question is governed by a great variety of circumstances.

We shall distinguish three fundamentally important aspects. These are the *absolute sensitivity*, the *relative sensitivity*, and the *practicability of detection*.

Absolute sensitivity is a property which we ascribe to those spectrum-lines of an element which appear in the source of light where the element occurs in the smallest quantity by which the element may be identified by spectrum analysis.

The absolute sensitivity is one which mainly concerns the qualitative side of spectrum analysis, the domain of which it is to detect the minutest quantities of an added substance or infinitesimal traces of impurities. The term "*absolutely sensitive*" applies accordingly to the *physically strongest lines*, that is, the first member of the principal series of the element, or in the case of doublets or multiplets in general their *physically strongest member*. Where the source of light is such that it chiefly contains positive atomic ions of the element, the basic line of the singly ionised spectrum (formerly referred to as the "spark-spectrum") may happen to be more intense than the basic line of the atomic spectrum (or "arc-spectrum"). Thus, for example, in the condensed spark between metallic electrodes the spectrum-lines of the ion, the so-called "spark-lines," are frequently more intense than the "arc-lines," *i.e.* the spectrum-lines of the neutral atom.

The preponderance of the spark-lines or that of the arc-lines is not only dependent upon the mode of excitation of the source of light but likewise upon the vapour pressure of the electrodes, and hence also

upon the nature of the primary substance of the samples which are subjected to analysis. Just as later on we shall consider the significance of the vapour pressure of the primary substance (that is to say, not that of the associated substance which is to be analytically determined) in its relation to the possibility of identifying it and the relative sensitivity, it behoves us to have regard to this factor in investigating the question of the absolute sensitivity. An example may serve to make this clear. A sample of lead and one of gold contained magnesium as an impurity. For its identification the authors employed the magnesium arc-line 2852, but they found in the case of the gold analysis the magnesium spark-line 2796 to have the greater *absolute* sensitivity. Whereas under the conditions of least Mg concentration in lead the line 2852 only was visible, this line in the case of the gold specimen disappeared at an earlier stage than 2796. This is indeed readily intelligible. Owing to the high vapour density, much vapour is present in the lead spark, hence the drop of potential in the spark-gap is small and the discharge partakes more of the character of an arc than is the case in the gold spark with its smaller vapour density. For this reason the arc-line of magnesium is that of greatest sensitivity in the lead spark, while in the gold spark it is the spark-line of the magnesium.

Notwithstanding this very clear state of our knowledge, one encounters in the older literature on the subject of chemical analysis by the spectrographic method observations—which are also correct—to the effect that these very basic lines are not the strongest lines. If we adhere to the definition propounded by de Gramont, according to which the ultimate lines of an element are those which are the last to disappear *in the source of light* as the proportion of the element is continuously diminished, it is correct to say that these lines are the basic lines. The discrepancy becomes intelligible when it is realized that the above definition loses its practical significance in the absence of data respecting the manner in which the luminous excitation is produced, the form and composition of the electrodes, and the spectrographic apparatus employed. All these are factors which may cause a basic line to practically lose partially or wholly both its character as an “ultimate line” as well as its significance for analytical purposes: in other words, it behoves us to distinguish between the energy of the spectrum-line derived from the source of light (*energy of emission*) and the “*effective intensity in the spectrum*,” which is the actual quantity subjected to measurement.

(b) ENERGY OF EMISSION AND ANALYTICAL INTENSITY

The energy of emission of a spectrum-line may be measured by the number of transitions made within a unit of time by an atom from a

higher to a lower state of energy and the duration of the luminous excitation. The transitions have their greatest frequency where they occur from the first stage of excitation to the normal state of the atom. The wavelength which arises from such a spontaneous transition, according to Bohr's frequency relation, is given by the difference of energy obtaining in the two atomic conditions. Neither the eye nor the photographic plate responds to the energy of emission; both do so only with respect to that amount of it which is thereby absorbed and used up in the secondary mechanism which serves for its detection and identification. The "analytical intensity" is therefore primarily governed by the properties of the instrument employed. Apart from the properties of the photographic plate, account requires to be taken of the quantitative variation of the radiation in the spectroscopic apparatus employed in the resolution of the aggregate light. All these are selective factors, that is to say, their magnitude is dependent upon the wavelength.

Ordinary photographic plates become insensitive above 5000 Å (*i.e.* beyond the green). They are highly sensitive—and fairly equisensitive—from the blue to right into the ultra-violet region, but their sensitivity markedly declines even at 2500 Å in consequence of the pronounced absorption which takes place in the gelatine wherein the silver bromide grains are embedded. With the advance into the ultra-violet region of short waves the absorption by the optical quartz components becomes increasingly pronounced, and the residual fraction of the intensity of emission which reaches the plate declines accordingly more and more. If, therefore, a basic line should happen to be situated too far into the long-wave or short-wave region it may well happen that the practicability of detecting it becomes much less than that of other physically weaker lines situated in more favourable regions of the spectrum.

By way of an example we may instance the case of cadmium. From de Gramont's tables it will be seen that the spark-line 2265 Å can be identified under circumstances of a much lower concentration than the spark-line 2144, although the latter has an intensity of emission which is twice as great. The excess of energy in line 2144 is more than balanced by the decrease in the sensitivity of the plate.

The source of light in itself is the seat of a process of decline, which is peculiarly conspicuous in the practical application of chemical spectro-analysis. The luminous portion of the spark is enveloped in a vapour cloud of the substance of the electrode. In this vapour cloud the concentration of the atoms in the primary state is greater than that of the ions or that of any of the energized atomic states. This cloud has to be traversed by the radiation. By the fundamental

discovery made by Bunsen and Kirchhoff an atom absorbs those very spectrum-lines which it emits, which is the well-known explanation of the Fraunhofer lines, and which furnishes the basis of the chemical absorption method of analysis of the stars. In the light of modern conceptions we prefer to say: Every atomic state absorbs those spectrum-lines which are emitted during the transition of the atom from any state into that state. Since the vapour cloud mainly contains atoms in the basic state those spectrum-lines which arise during the reversion to the basic state will be those which are absorbed most, that

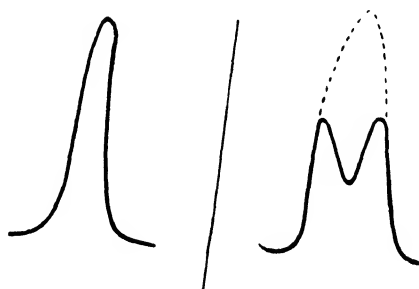


FIG. 1.—Emission line
without | with self-reversal.

is, precisely the basic line. With a spectrum apparatus capable of producing a sufficiently great dispersion these lines are frequently seen to exhibit the phenomenon of “self-reversal.” Within the cloud of vapour the middle of the invariably distended spectrum-line undergoes absorption, so that one apparently observes two closely adjacent spectrum-lines (fig. 1). This signifies that the basic lines become weakened in a measure as the absorption in the vapour cloud increases in intensity, which in its turn is mainly governed by the thickness and density of the vapour. It is an easy matter so to arrange a source of light that the basic line cannot be seen at all or only very faintly. Thus by far the most intense Hg-line 2537 of the spectrum of a *heavily loaded* mercury vapour lamp is frequently entirely absent in the spectrum. It is, on the other hand, difficult, often impracticable, to produce a source of light in which the basic lines are not markedly weakened by this species of absorption. The use of the basic line for the purposes of quantitative analysis is therefore not free from misgivings (see further observations on this subject in the discussion of the “relative sensitivity”).

A further circumstance which frequently causes the intensity of the basic lines to fall below that of other spectrum-lines arises where the dispersion of the apparatus used does not suffice to separate the whole of the spectrum-lines, especially the stronger ones. In this connection

we will only instance one case.¹ In the so-called first secondary series of zinc every "spectrum-line" forms a multiplet due to the splitting up of the atomic state into several closely allied energy levels. Each of these multiplets consists of six lines. In the table the first column gives the wavelengths and the second their relative energies of emission. The brackets in the second column comprise those lines which fail to be resolved in a spectrograph of intermediate size. At 3345 three spectrum-lines are superimposed and at 3303 this is the case with two. The blackening of the plate where these lines occur

WAVELENGTHS	ENERGY OF EMISSION	APPARENT INTENSITY
3346.0	5	9
3345.6	3	
3345.1	1	
3303.0	3	4
3302.7	1	
3283.4	1	1

may thus readily enough be stronger than it is at the basic lines. As a matter of fact, for the analytical estimation of zinc, likewise of cadmium and mercury, the first member of the secondary series is better adapted than the basic line of the principal series, for in all but excessively low Cd-concentrations the latter is invariably fainter. Nevertheless, for the detection of minutest traces the basic line of the arc-spectrum presents the highest degree of sensitivity, notwithstanding the superimposition of the triplet lines.

(c) THE PRACTICABILITY OF DETECTION

Apart from the circumstances just referred to, others enter into consideration, which we shall comprehend into the question of the practicable limits of the detection of a spectrum-line. By this we refer to the conditions under which a spectrum-line may be recognized on the finished photographic plate so as to be able to infer from this the presence of a certain element in the source of light.

The limits set to the possibility of detecting a spectrum-line are due in all cases to the same cause, which is that the line disappears in the photographic base upon which the spectrum is formed, that is, in the blackened emulsion, which in a minor part owes its origin to diffuse light (due to faults of the optical material), but in the major part to molecular bands (occasionally also to the thermal luminosity of minute incandescent particles) in the path of the spark. This band

¹ Respecting a discussion of other examples the reader is referred to the paper of W. Gerlach in the *Zts. f. anorg. u. allgem. Chemie*, 142, 383, 1926.

emission of the spark is never entirely to be obviated. It is made up of the emission from molecules derived from atoms of the electrode material and the oxygen of the air, the hydrogen, the moisture which may be present, the polyatomic molecules of the electrode material (Cu_2 , Ag_2 , Sb_3 , etc.), and finally the bands of the atmospheric gases.

In the case of solution sparks very pronounced bands of 'water vapour' arise as well.

In the event of a spectrum-line being situated in an intense portion of such a band, it will be useless for quantitative analysis, and it is in such a case immaterial whether it can be seen or whether it disappears in the bands. For even if it is visible its intensity will fail to furnish a measure of the concentration owing to the inconstant intensity of the bands, and any attempt to compare its intensity relatively to that of some other line with a different background is then utterly futile.

It will now be quite clear why "ultimate lines" are not necessarily in every case those endowed with the greatest sensitivity in the service of qualitative analysis. We have seen that they fail in this respect when they happen to fall into a region where their detection is obscured by other factors. For this also we will submit an example. Thus, in the analysis of cadmium the group of lines 3614, 3613, 3610 (which in most cases coincide) is of great importance, yet in the spark-from-liquid mode of analysis it proves utterly useless, and similarly the magnesium lines 3832, 3838, since it so happens that they arise in the heaviest water vapour bands at 3600 and 3800.

It is indeed practicable so to modify the source of light by an appropriate choice of the conditions of discharge as to reduce the band emission. Unfortunately, suitable conditions of the spark are frequently productive of unfavourable conditions from another cause, since the intensity of the bands diminishes in a measure as the temperature of the spark rises, while at the same time the capacity in the spark circuit is increased and the *damping* of the discharge diminished; but in these circumstances the electrodes become heated, and the quantitative value of the analysis may thereby be falsified. In the event of the electrodes being actually rendered incandescent by the increase of the energy the bands become extremely intense, from which it follows that there is a limit to the increase of the energy. Under normal conditions of discharge between metallic electrodes, to give an instance, the intensity of the *atmospheric band spectrum* is largely influenced by the *vapour pressure of the primary substance of the electrodes*. When the vapour pressure is low, and the passage of the spark impeded, it will be necessary

to give longer exposures in order to ensure the formation of sufficiently intense spectrum-lines of the metal, and this in its turn causes the intensity of the air bands (and also that of the "air-lines," *i.e.* the spectrum-lines of the dissociated oxygen and nitrogen) to increase in a pronounced degree.

To illustrate this we append an example of a case in point arising out of the use of solid and liquid electrodes :

ELECTRODES		VAPOUR PRESSURE	REQUIRED TIME OF EXPOSURE	BANDS	FORM OF SPARK
Solid	Lead in Gold	Low	Long	Intense	Narrow discharge surface
	Lead in Cadmium	High	Short	Faint	Broad discharge surface
Liquid ¹	Lead in the form of its chloride	Low	Long	Intense	Small aureole ¹
	Lead in the form of its nitrate	High	Short	Faint	Large aureole

Lead is more readily detected, *i.e.* is analytically more sensitive in cadmium since, in view of the higher vapour pressure of cadmium, the path of the discharge is more richly laden with metal vapour than is the case with gold sparks. Under the conditions of the method "normally" employed by us the presence of lead in cadmium, tin, and bismuth was identifiable in concentrations which were 30 times lower than in the case of gold. Tin proved identifiable in magnesium at 0.005 per cent. by atomic weight and in lead at 0.0005 per cent. by atomic weight.

We have made experiments in order to ascertain whether the interference occasioned by the presence of bands could be diminished by generating the spark in the rare gas argon instead of in air. For this purpose we employed the tube illustrated in fig. 11. The result achieved thereby was not particularly notable. In the first place, it is a very difficult and costly matter to always employ pure argon, and secondly the spectrum of argon with its many lines is likewise induced and thereby contributes a complicating factor which is difficult to eliminate.

There is a means whereby the interference arising from the presence of bands may be largely eliminated, and that is the use of a spectrum apparatus of very great dispersion. The value of a high dispersion

¹ Details respecting the sparks from liquids will be found on pp. 39 *et seq.*

arises from the fact that the bands which present the appearance of a continuous darkening are in reality made up of a large number of very closely packed and frequently inherently faint spectrum-lines, which are thus resolved. Where the dispersion is sufficiently great so that the lines of the band appear clearly separated, the background becomes clear by reason of its diminished intensity, or the lines of the band may become so far separated that the spectrum-lines of the element once more become visible. Whilst obviously spectrum apparatus giving very large dispersion is not adapted for practical analysis arising in technical operations, it is on the other hand inexpedient to employ for this purpose apparatus which furnishes too small a dispersion. The latter should be such that the light-transmitting capacity does not become so small as to demand excessively long times of exposure.

The limits of detection might conceivably be governed by a second cause. As the concentration of an element diminishes the intensity ultimately becomes so small that energy impressed upon the plate fails to produce photographic blackening, so that the "threshold value" of the emulsion is not reached. This threshold value is further increased by the circumstance that the luminous process by reason of the intermittency of the spark discharge, is not continuous in relation to time. ("Intermittency effect" of the photographic plate.) It would seem, however, that with the forms of apparatus employed for practical analysis the practicability of detecting the emission of a spectrum-line is not subject to this circumstance, but is solely governed by the photographic coating.

(d) THE RELATIVE OR CONCENTRATIONAL SENSITIVITY

While for qualitative analysis a knowledge of the absolutely sensitive lines is an important requirement, the quantitative determination of the proportion of an element present in a sample demands recourse to lines of *great relative sensitivity*, that is to say *the variation of the intensity of the spectrum-lines referred to in relation to the variation of the concentration*, i.e. $\frac{\delta I}{\delta K}$ should have the greatest attainable value. We

ourselves have not carried out systematic experiments in order to ascertain to what extent different spectrum-lines of an element have like or varying relative degrees of sensitivity.¹ It has, however, struck us as an interesting fact that all spectrum-lines which are emitted by transitions to the lowest energy level of the atom have a very small relative sensitivity. *On the other hand, we have ascertained by systematic tests that the relative intensity of a given spectrum-line of an*

¹ In Chapter V, p. 101, this question will be dealt with in conjunction with our own experiments.

element is independent of the primary substance and added substances (cf. this chapter, section e).

We have seen above that the *intensity of the basic lines* of an element diminishes in a measure as the vapour cloud about the source of light becomes larger and denser. If now the concentration of the element in the source of light diminishes, the true intensity of emission declines by reason of the diminished number of the luminous atoms. At the same time, however, the intensity of the absorption diminishes. Hence, despite a pronounced diminution of the concentration the intensity is often found to undergo little or no decline in its intensity. It may even happen that the observed intensity for a time increases as the concentration diminishes. Owing to the mutually opposite effects of emission and absorption *the basic lines have accordingly a small relative sensitivity*, which moreover is not independent of the primary substance. It is only *at very low concentrations*, where the absorption within the vapour cloud ceases to play any important part, that *these lines become available for the purposes of quantitative analysis*. Pertinent examples, which are frequently encountered, are furnished by the basic doublets of copper, silver, and gold. The basic lines of the spark-spectrum likewise behave exactly as do the basic lines of the neutral atom.¹

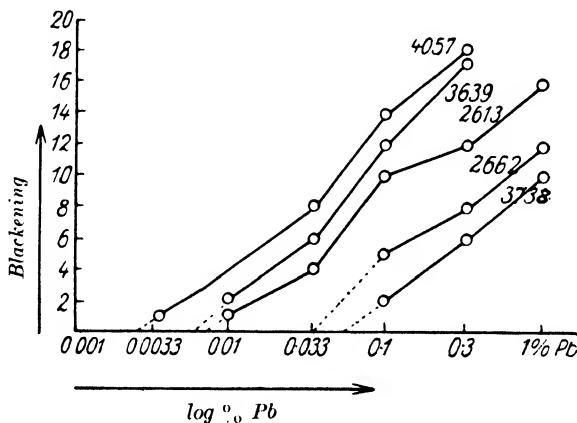


FIG. 2

We are cognisant of only one systematic investigation concerned with the comparison of the relative sensitivity of different spectrum-lines of an element. A Reis² has investigated the effects of sparks between lead nitrate solutions, while maintaining with the utmost care uniform conditions of discharge. Fig. 2 represents the blackening effect

¹ cf. Note No. 1 to Table I, p. 75.

² A. Reis. Die Naturwissenschaften. 14 (1928), 1114.

as a function of the concentration. It shows that the relative sensitivity is approximately the same for these five lead lines. When solid electrodes are substituted for the solutions the relations between the intensity of the lines and the Pb content are "similar" (according to Reis) to those obtaining with aqueous solutions.

Nevertheless, it is *not practicable* to establish, on general principles, an *absolute system of analysis* which is solely based upon the *measurement of the intensity of spectrum-lines* of the element which is to be quantitatively determined.¹

In the beginning of this chapter we already had occasion to point out the significance of the nature of the source of light in relation to the intensity of the spectrum-lines of the elements present in the source of light. The significance to which we thus alluded is not by any means confined to the manner of the "excitation of the spark" or the "excitation of the arc," with which alone we were there concerned. In the introductory chapter we discussed this in reference to the excitation of the spectrum-lines of the rare gases of the air. One must, however, take into consideration the fact that for physical reasons the intensity of luminosity of an element will depend upon the nature and quantity of the other elements associated with that of the electrodes.² A particularly significant influence is exercised by the circumstance that where the combination of the elements in the electrodes differs, the internal conditions of the spark, and therefore the conditions of the luminous process, even under like external electrical conditions, are never entirely alike. Hence it is not practicable to establish a generally valid numerical relation between the intensity of the ultimate lines and the concentration or the limiting concentration at which the ultimate lines can be detected. For this reason tables giving the limiting concentrations at which an element can yet be identified are devoid of foundation, just as graphic representations of the photographic blackening of a spectrum-line as a function of the concentration of an element in a source of light are useless for *practical* purposes.

A reflection, quite similar to that applied to the question of the conditions which render detection practicable, may render this apparent. At the outset we shall make a supposition, though actually in itself it is scarcely realizable, inasmuch as we shall assume that the spectrograms which will be discussed in what follows are produced throughout under precisely identical conditions in the matter of electrical discharge and time of exposure, and that the plates are treated in a perfectly uniform

¹ In special circumstances of the solution method of analysis an absolute method by the measurement of the intensity would appear to be practicable. (Gromann, *Zeitschr. anorg. u. allg. Chemie* 180 (1929), 257.

² We shall revert to this question when showing that this influence has no bearing on our method of analysis.

manner. We proceed to take a series of spectrograms of a primary substance P_1 , which contains a, b, c, \dots of an admixture A . The blackening of the A -lines depends upon the concentration and, other things being equal, it is determined by the number of the A -atoms which are luminous during the time of exposure, and this number in its turn will be proportional to the concentration of A in P_1 . The degree of blackening of the A -lines is measured. The same admixture A is now associated in the same concentration as before with another primary substance P_2 . The intensity of the A -lines in this P_2 set of spectrograms, *i.e.*, whether it is equal to, greater, or less than that obtaining in the P_1 set of spectrograms—that is to say *the number of the A -atoms—depends upon the ratio of the respective vapour pressures of the primary substances P_1 and P_2 and in no way upon the vapour pressure of A .* This is because P_1 and P_2 volatilize, and during this process as many A -atoms are carried into the luminous track as there are in the volatilizing quantities of the primary substances.

The establishment of a method of absolute analysis might thus conceivably be derived from the known numerical value of the relative sensitivity of a spectrum-line, if it were practicable to so regulate the quantitative conditions as to make the spark vapour invariably contain the like number of atoms of the primary substance. This, however, is wholly impracticable, so that an analysis of this kind is not conceivable.

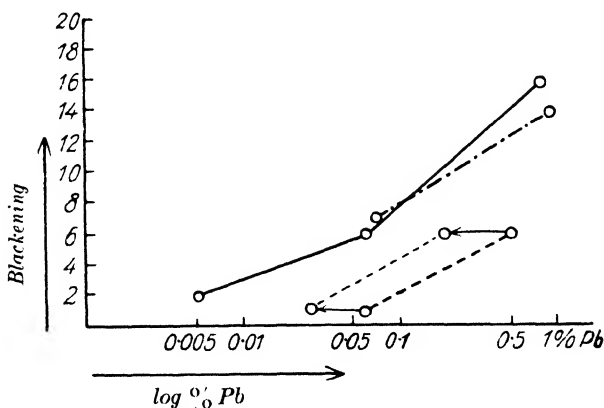


FIG. 3. — Gold, - - - Au + 10% Cu, Copper.

That nevertheless a single verification of this relation between intensity and concentration may be of considerable importance we have already had occasion to emphasize in connection with the investigation of the relative sensitivity of different lead-lines as carried out by A. Reis. The same investigation by Reis also furnishes an example which shows that it is never admissible to generalize these absolute

measurements. Maintaining uniform external conditions and the same times of exposure, the intensity of the spectrum-line 4057 Å of lead was measured as a function of the lead content when lead was added to pure gold, to an alloy of 90% by weight of gold and 10% by weight of copper, and to pure copper. With equal proportions of lead throughout, it was found, as indicated in fig. 3, that in gold the blackening of the lead-lines was more intense than in copper. The presence of the 10 per cent. of copper was still without influence. To begin with, the result of observation obtained for pure copper requires to be reduced by calculation since the lead content is stated in percentage by weight instead of in atomic percentage. This reduction is necessary since the luminous excitation is governed by the number of atoms, *i.e.* the concentration of the atoms in the source of light and hence also in the substance of the electrodes. 1 gramme of lead contains approximately the same number of atoms as 1 gramme of gold, but only about one-third the number as compared with 1 gramme of copper. Given like concentrations by weight, the atomic concentration of lead in copper is roughly three times smaller than it is in gold, so that the lower curve requires to be shifted to the left. Whilst thus the difference becomes very much less, it does not vanish entirely, and doubtless it arises from the fact that the spark transit between the easily oxidizable copper electrodes is invariably more irregular and more difficult to induce than between gold electrodes, in consequence of which the quantity of luminous vapour formed in a like time of exposure becomes lessened. Nevertheless it is significant that in this case also the relative sensitivity for gold as the primary substance is the same as that for copper as the primary substance. In the following section we shall give an account of our own investigations in this connection. The application of a known relative sensitivity for the purpose of analysis will be discussed in Chapter V, *g*.

(e) THE MUTUAL INDEPENDENCE OF THE CONCENTRATIONAL SENSITIVITY AND THE PRIMARY AND ASSOCIATED SUBSTANCES

In the preceding section we have shown that the absolute intensity of an *A*-line depends within very wide limits upon the nature of the primary substance which contains the admixture *A*. In the present chapter we shall discuss the absence of interdependence between the concentrational sensitivity and the nature of the primary substance *P*.

We shall in the first instance proceed to describe the method employed by us for the purpose of comparing the concentrational sensitivity of the spectrum-lines of an admixture *A* in different primary substances P_1 and P_2 . Alongside the spectrum $P_1 + p\%A_1$ we photograph the spectrum of $P_2 + p\%A_1$, giving a time of exposure such that

the A -lines 2 situated one below the other may have equal intensities in both spectra a and b (fig. 4). Let P_1 and P_2 be tin and bismuth respectively. When this identity of intensity obtains, all other spectrum-lines will likewise be of equal intensity in pairs (3, 4, 8, 9). We may now bring the two spectra of the primary substances P_1 and P_2 into mutual relationship by singling out two lines P_1 and P_2 of equal intensity, appertaining to the primary substances. If now, under like conditions and while maintaining the identity of intensity of

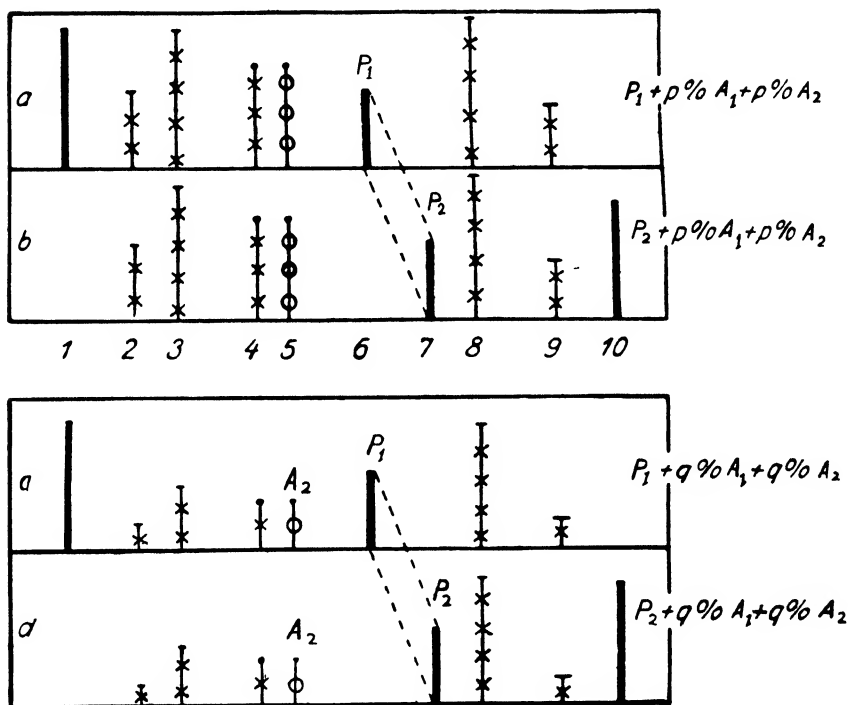


FIG. 4

P_1 and P_2 , we photograph the spectra c and d of $P_1 + q\% A_1$ and $P_2 + q\% A_1$ ($q < p$), arranging them side by side as before, we find again that the Z -lines 2, 3, 4, 8, 9 in the two spectra c and d present equal intensities, which signifies that the corresponding A -lines have like concentrational sensitivities. Despite large differences in the absolute intensities of the A -lines which arise when P_1 and P_2 happen to be substances with widely differing vapour pressures, the relative sensitivity (but not the absolute sensitivity) of the A -lines maintains its independence of the primary substance. We have thus carried out these experiments both with cadmium and tin as well as with tin and gold

by way of the primary substance (see also p. 121). Respecting the application of the relative sensitivity for very general analytical methods the reader is referred to Chapter V, *g*.

The condition that a basic or absorption line (8) in the spectra $P_1 + n\%A_1$ and $P_2 + n\%A_1$ shall be of like intensity is likewise fulfilled in *a*, *b* and *c*, *d* (*e.g.* for bismuth and tin taken as primary substances). As explained above, the absorption line is at once recognizable by the fact that its intensity gradient is small. In the event of P_1 and P_2 not being bismuth and tin or cadmium, or lead, in fact not substances having approximately similar vapour pressures in the spark but such as have entirely different time-rates of volatilization in the electric spark, such as cadmium and gold, different conditions of discharge will obtain, despite the uniformity of the external arrangement. The basic lines (8) will then undergo in P_1 and P_2 various degrees of self-absorption and hence will exhibit abnormal appearances, as we have already emphasized above.

Where the different lines of an added element *A* belong to a like series of spectra, or where they are members of a multiplet, it follows that the diminution of the intensity which goes hand in hand with descending *A*-concentrations is quite generally the same in degree for all these lines and entirely independent of the primary substance.

Where the primary substances P_1 and P_2 contain two admixtures $p\%A_1 + p\%A_2$ it has been found that these two admixtures likewise have equal concentrational sensitivity, as may be seen from a comparison in fig. 4 of the pair of lines 4 (A_1) and 5 (A_2).

CHAPTER III

THE ELECTRICAL AND OPTICAL APPARATUS EMPLOYED
IN ANALYSIS BY THE EMISSION SPECTRUM

In this chapter we shall discuss the instrumental devices and experimental arrangements employed in the practical application of the spectrographic method of chemical analysis. On the one hand, we shall confine ourselves to the appliances devised for the production of the important *spark-spectra* since other modes of generating spectra have been sufficiently dealt with in the available literature. On the other hand, we shall concern ourselves with those instrumental appliances which we have thoroughly tested by our own experience and found to be well adapted for the purposes of our methods.¹

(a) THE HIGH-TENSION GENERATOR

The first problem which presents itself is to realize the appropriate conditions for a suitable electrical spark. The fundamental requirement may be stated thus : The line-spectrum of the electrode material should be subjected to the most intense degree of attainable excitation, while the atmospheric spectrum should vanish as far as possible.

For the purpose of generating a high-tension spark current there are two fundamentally practicable sources, either of which is capable of application in a special way, according as the primary current is of the alternating type or an interrupted continuous current. An arrangement fed by a *continuous current* may be given the preference where, without lowering the tension and the momentary energy in the secondary circuit, it is required to *avoid heating of the electrodes*; for in this system it is an easy matter, by regulating the frequency of interruption, to introduce sufficiently long cooling pauses between the successive spark passages. More especially, however, it is the form of the curve of the secondary voltage of a sparking coil operated by an interrupted continuous current which offers the assurance of an effective interruption of the spark current and thereby in itself an adequate measure of cooling. A characteristic feature of the D.C. sparking system is the sudden interruption of the primary current and the very high load in the spark which obtains during this very short period.

¹ We have endeavoured to adapt the extent and mode of the exposition to the requirements and a reasonably assumed initial knowledge of the chemists and engineers who are mainly concerned with the work discussed in this book.

The performance of a D.C. spark apparatus is therefore determined by the nature and quality of the *interrupting device*. Uniformity and constancy over a prolonged period are primary requirements. The ordinary Wagner hammer and also the Deprez interrupter are useless. Electrolytic interrupters (Wehnelt, Simon) bear a larger energy load, though to this end they require to be so set as to impart a very high inherent interruption number (200 to 2000 per second), which may be rendered variable by introducing an adjustable self-induction in the primary circuit; for, unless it be so set, it does not interrupt with uniform rapidity, hence the risk of overheating the electrodes is very great. It should be noted that for every energy value there is a critical number of interruptions. Nevertheless, owing to their small initial cost, these interrupters are very useful for many investigations carried out with improvised arrangements.

The only truly efficient interrupter devices adapted for continuous working, we should think, are the so-called "rotary mercury interrupters." The principle upon which these work is that a current-bearing stream of mercury hurled from a rotating jet is made to impinge upon one or more stationary points of contact during each revolution. The stream is hurled through petroleum or coal-gas, whereby good cooling of the contact is obtained. The interrupter should be given dimensions far exceeding those actually required in order that for its size it may be only lightly loaded. It will then work more uniformly and need cleaning at far less frequent intervals.¹

An *alternating current*, on the other hand, offers facilities for impressing far greater energies, and has the advantage that it gives very uniform running of the spark. For producing spectrographic records with a solution spark-gap the A.C. system is therefore well adapted, especially for dilute solutions, but likewise for investigations of metals with high melting points with respect to admixtures having likewise high melting points.

In our *D.C. set* we employ by way of an induction sparking coil an open transformer made by Klingelfuss (of Basle), in which the number of primary windings may be optionally increased and diminished and the secondary coil of which is made up of separate coils, which may be combined as may be required. The current interrupter takes the form of a rotary mercury-petroleum interrupter actuated by a shunt-

¹ We give preference to the mercury-petroleum interrupter. When this interrupter ceases to work uniformly it should be taken apart. The irregular working will be found to be due to the accumulation of a thick emulsion of mercury, petroleum and carbon, from which the mercury may be easily expressed by mechanical means (for instance with the aid of a porcelain pestle in a porcelain basin). The mercury will then collect and may be drawn off. The residue may be retained and the last traces of mercury extracted from it by heating when a sufficient quantity has accumulated.

motor and bearing on its spindle a fluid revolution indicator. The point of interruption has a large condenser connected in parallel with it to obviate sparking, that is, for the purpose of rendering the interruption as spontaneous as possible. Great care should be taken to maintain a constant rate of interruption. A suitable arrangement of the apparatus and electrical connections is shown in fig. 5.

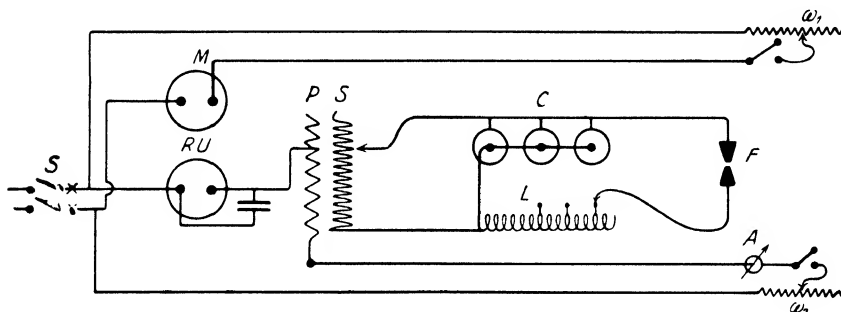


FIG. 5.—*M* motor to the rotary interrupter *RU*, *PS* open induction coil; *C*/*L* capacity and self-induction in the spark circuit *F*

A convenient disposition of the *A.C. apparatus* is indicated in fig. 6, as supplied by the Transformator-fabrik Magnus, of Nuremberg. The primary P.D. in this apparatus is furnished by an A.C. of 110 volts. Where this voltage is not available a step-down transformer should be put in series with the primary. We have invariably done so in order to be able to operate at any time with a primary of 110, 90 or 70 volts as a means of varying the magnitude of the energy. A closed metal casing contains the transformers suitably connected (step-up ratio 110/15000 volts), a Leyden jar, and a variometer (for the self-induction). Externally the apparatus bears the

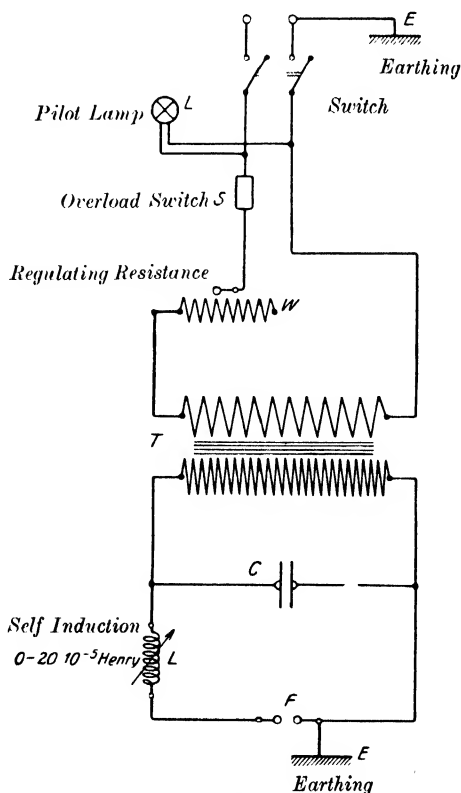


FIG. 6

regulating resistance to the primary load, switches, amperemeter and voltmeter for measuring the primary energy. Since the self-induction furnished by the variometer is rather small, we instal in the spark circuit as a rule an additional self-induction of about 0.0002 henry.

It is important in the various experimental arrangements to have the switches and regulating resistances so disposed that they may be controlled from the place where the operator sets the spectrograph. Also the switchboard instruments should be within sight from this point.

In the matter of the choice of the conditions of discharge two fundamentally different modes of spark discharges may be distinguished—viz. the condensed discharge and the non-condensed discharge. The former has an oscillatory character, while the latter is non-oscillatory.

An uncondensed discharge results when the ends of the secondary spool of the transformer or of the induction coil are led directly to the spark-gap without introducing capacity. An individual discharge in this case consists of a single current transmission through the stratum of gas which separates the electrodes. In these circumstances it is almost exclusively the atmospheric spectrum which is excited. The spark is enveloped in an aureole and resembles rather a flame (it is for this reason not inaptly referred to as a “high-tension arc” or “spark-flame”). The spectra of the alkalis and alkaline earths are readily obtainable—as in the flame—when the salts are introduced into such a path of discharge.

In the condensed mode of discharge a large capacity is put in parallel with the transformer. This capacity is then charged up and discharges across the spark-gap when a sufficiently high potential has been reached. The high-frequency spark current carries large quantities of electricity to and fro. During this process the excitation of the atmospheric spectrum is accompanied by the line-spectrum of the electrodes, and the intensity of the latter increases with the magnitude of the capacity which has been joined in parallel to the transformer. At the same time the brightness and crackling noise of the spark becomes augmented. In order that the regularity of the spark discharges may be maintained at a high capacity the length of the spark-gap requires in some cases to be shortened by an appropriate amount. By way of a capacity we employ a battery of 3 to 4 Leyden jars, each having a capacity of 3000 cm.¹ The undesirable atmospheric spectrum is eliminated by the introduction of the *self-induction*, or at least it is very considerably reduced. The *magnitude of the self-induction is of very great significance* in that upon it depend in a great measure the resulting intensities in the spectrum. Especially in difficult cases of

¹ The jars of Schott & Gen., Jena, are particularly recommended.

qualitative analysis, variations of the self-induction should be resorted to. The self-induction in our experimental work consisted of a spool of 10 cm. diameter and 150 turns wound in two layers. The spool should preferably be furnished with a number of tappings for the purpose of effecting a convenient variation of the self-induction. The capacity and self-induction are insulated with respect to earth, for instance by placing them upon a stout plate of glass. Similarly all high-tension leads should be conveyed through glass to ensure good insulation and yet be visible.

(b) SPARK-GAP FOR SOLID ELECTRODES

The spark-gap apparatus should be very substantially made and should be so designed that the electrodes may be readily interchangeable. It should moreover render it an easy and certain matter to ensure the formation of the spark in an accurately unvarying and at all times reproducible position. Much time would be wasted if every fresh specimen necessitated a re-adjustment. The spark does not at any time remain in the same spot on the electrode; it should, however, only oscillate in the direction of the optic axis of the collimator of the spectrograph. The spark stands which are suitable are that of de Gramont, the one devised by us, or some other happily improvised arrangement. Our spark-gap apparatus is shown in fig. 7. Its chief advantages may be briefly stated thus: (1) The clip pieces move symmetrically with respect to the optic axis by the action of a right-and left-handed screw thread. (2) The upper electrode-holder is mounted in a ball- and -socket joint: for the purpose of interchanging electrodes quickly and with precision it is expedient to first turn aside the upper electrode-holder; with the aid of the ball-joint it may subsequently easily be set back to its original position. The reproduction of the position of the electrode ends is obtained with the

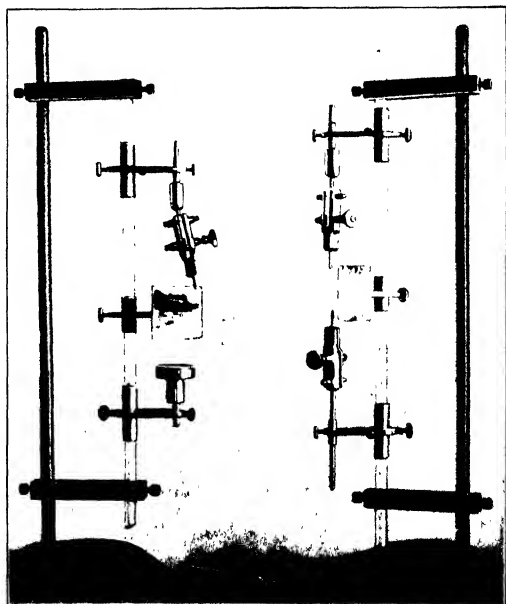


FIG. 7

aid of two reflecting measures or two shadow images of the electrodes. (3) In the place of the lower metal electrode a liquid electrode may be readily substituted in the manner described on p. 41, fig. 13.

The choice of suitably formed electrodes is ruled by the following considerations :

- (1) The spark should oscillate exclusively in the direction of the optic axis.
- (2) The surfaces taking part in the spark discharge should not become unduly heated (*i.e.* the spark must not be allowed to pass continuously between the same points) : and
- (3) The electrodes should be such that they may be conveniently produced from the available material. Incidentally it should be practicable to satisfy the further condition that little or no material is to be wasted.

Fig. 8 shows a number of appropriately shaped electrodes of different spark discharging material, the upper end of the sketches in every case representing that from which the spark emanates. Thick wires should be cut off with pliers (*a*), sheets cut into rectangles (*b*), thin wires bent into loops (*c*), and thick cylindrical rods cut into discs (*d*). Bars and blocks furnish suitable electrodes by cutting off specimens of the kind shown at (*e*). The electrode surfaces should be free from points and jags, and should be as smooth as possible. Failing this, the spark attaches itself to these points and gives rise to local heating. The conditions under which the discharge takes place thereby lose their constancy, band-spectra arise in greater intensity—the intensity of the air-lines is liable to vary—so that it is often impossible to distinguish air-lines from the lines of an admixture in the electrode,

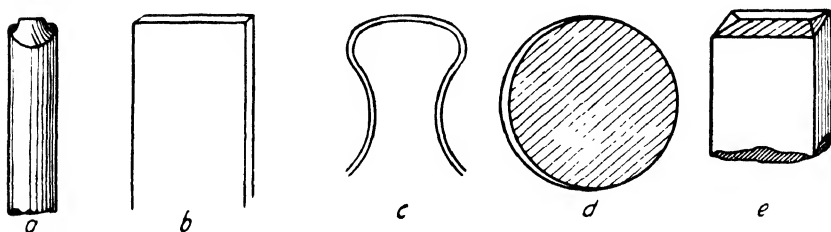


FIG. 8

especially in qualitative analysis. Finally it may easily happen in these circumstances, that volatilizable associated substances are distilled out, in consequence of which the intensity of the spectrum-lines might greatly exceed that conforming to the actual degree of concentration (see pp. 60 and 61). All these contingencies should be rigorously taken into account where a special analytical investigation does not

admit of the choice of one of the electrode forms $a-e$, and where, for instance, jagged fractures are to be subjected to analysis.

The length of the electrode surface is in itself a matter of no moment. Where the specimens admit of it, we take lengths ranging from 3 to 10 mm. The distance between the electrodes (*i.e.* the spark-gap) is usually about 2 to 3 mm.

The manner in which minute specimens may be applied may be illustrated by the following example. A wire of very pure gold of a thickness of a few millimetres should be excavated at the end in the manner shown in the sketch (fig. 9). It should then provisionally be thoroughly sparked in order to remove any contamination occasioned by contact with working tools (notably steel). The cavity should then be made to receive the very small specimen and secured therein by burnishing after the manner of a mounted jewel. The opposite electrode should then likewise be purest gold. The spark will then pass directly over to the point of the specimen. The reason why gold should be chosen as a mounting medium is that its vapour pressure should, where at all practicable, be less than that of the mounted specimen.

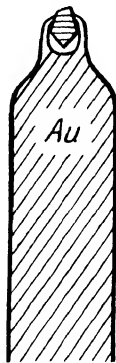


FIG. 9

Very small quantities of metallic powder or traces of metallic mud (also dissociable traces of a metal salt) should be moistened, rubbed down with very little filter paper, after which a pellet should be made of it and thrust into a glass tube slipped over the lower electrode in the manner shown in fig. 10. In some cases it is expedient to add to the water used in the preparation of the pellet a trace of sodium chloride in order to increase the conductivity. In other cases the metallic powder may, by way of an example, be fused into cadmium.

In many cases it is desirable to let the spark discharges take place in an atmosphere of a neutral gas instead of in air. A simple spark-gap devised for this purpose is shown in fig. 11. The device is made of blown glass throughout, and in front bears a quartz window for the emission of the radiation. The electrode-holders are movably attached to the glass arms on either side, and are joined thereto by air-tight rubber sleeves. The gas enters through a glass tube and streams directly upon the middle of the spark-gap, and cools the electrodes, thanks to its continual and rapid renewal.

(c) SPARK-GAPS FOR DISCHARGES FROM SOLUTIONS

We now proceed to describe *spark-gaps* such as we have employed for analyzing *metal salt solutions*. Where it is solely a matter of qualitative analysis very pure carbon electrodes may be saturated with the

solution, or the lower electrode of a spark-gap made up of carbon rods may have a cup-like hollow bored in it for the reception of the fluid. In the spectrogram due attention should then be bestowed upon the degree of purity of the carbon. With an arrangement of this kind it is in certain cases practicable to qualitatively detect smaller traces than

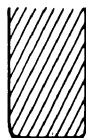


FIG. 10

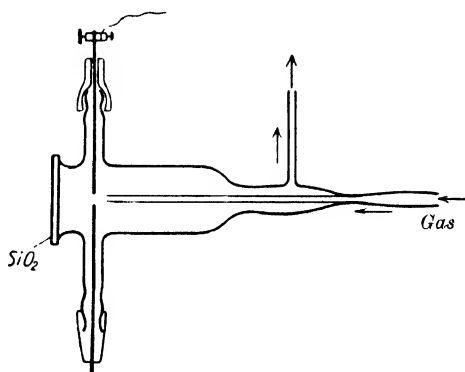


FIG. 11

can be done with the spark-gaps which we are now about to discuss. On the other hand, they are particularly well adapted for exact *quantitative* analysis. The spark-gaps employed for this purpose should be exclusively of a kind in which *the spark can only leap from a metal electrode directly upon the free surface of the solution*. One of the spark-gaps which we use is shown diagrammatically in fig. 12. The lower electrode consists of a narrow glass tube furnished with a funnel *G* for the introduction of the solution at one end. The other end is blown into a small sphere *K* having in the middle of the top a circular opening of a width of 4 mm., through which the liquid oozes out by its capillary meniscus *F*. A platinum wire, which at *D* is fused into the narrow tube and admits the current, terminates with its fused-on thickened end *M* in the centre of the sphere *K*. The upper positive electrode consists of cadmium, which is protected from the corrosive influence of strong acid vapours by being sealed in a glass tube whence it protrudes with its lower wedge-shaped end. Current is admitted by a copper wire fused into the cadmium. The whole is encased in a protecting tube with a

tubulure *A* for the emergence of the radiation. The liquid which flows over at *F* collects in the dish placed under the tube.

The spark-gap has a large resistance of distilled water¹ joined in series with it. The spark with its small quantity of energy then leaps directly over upon the meniscus *F* of the fluid without spraying, in fact without producing any deformation of the meniscus. If the resistance be entirely removed the liquid meniscus disintegrates spontaneously, and the spark leaps over directly to *M*. Where the resistance is very great the spark will be faint, and in that case the bands wholly surpass the line-spectrum in their intensity. By the addition of a very few drops of dilute hydrochloric acid to the series resistance, we reduced the resistance until the spark markedly sprayed the liquid, while still terminating at the surface of the meniscus. The line spectra of the dissolved metals then became considerably more intense in brightness in comparison with the C'd-lines and the bands.

In the second arrangement it becomes practicable to turn to account the whole of the available energy of the spark current. It is therefore, according to our experiments, the one which is chiefly to be recommended. It is preferably oper-

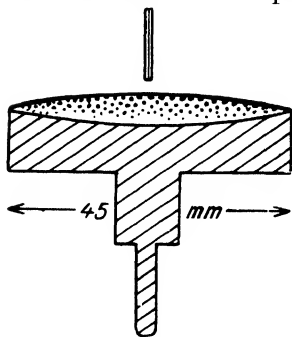


Fig. 13

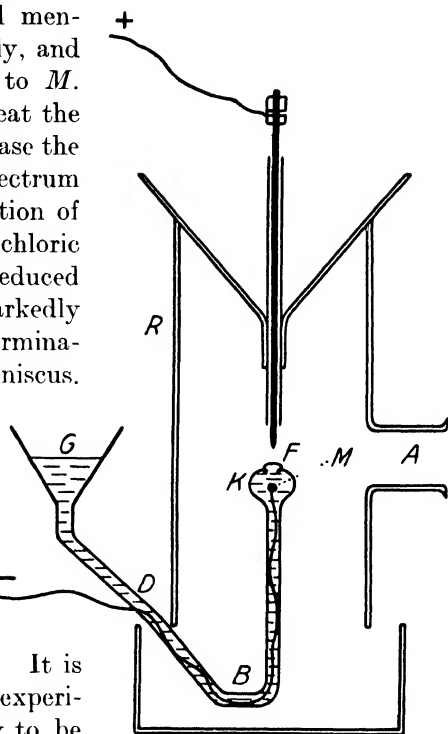


Fig. 12

ated by the A.C. apparatus described above, using it with the full measure of the available energy. The liquid electrode (fig. 13) is in the form of a circular metal dish 10 mm. thick and having a spherical concavity 2 mm. deep. and 45 mm. in diameter. This cavity is lined with platinum foil or thickly gilded, and should be filled with the solution until the meniscus of the liquid stands 1-2 mm. above the level of the periphery

¹ F. Gromann, Z. für anorg. u. allg. Chemie, Vol. 180, p. 257, 1929, where also will be found described a spark-gap for solution sparks.

of the dish. The latter is accommodated in the lower holder of the spark stand (fig. 7). With this arrangement the spark may be passed with much greater energy and terminates noisily but *without any appreciable amount of spraying* from the liquid surface opposite the solid electrode, where it spreads out to the extent of a few millimetres into a vigorously oscillating aureole and finely radiated sparklets. The time-rate of volatilization in the spark itself is very great, so that in strongly acidulated solutions the hydrogen chloride is evolved in small bubbles. As soon as the dish is reduced in size ramifications of the spark may be seen to leap over to the rim along the surface of the liquid, especially in the case of badly conducting liquids.

The previously described arrangement of the spark-gap, with water resistance in series with it, has the following notable disadvantages :

- (1) The occurrence of intense air and water bands in the spectra of the solutions in the long-wave ultra-violet region up to W.L. 3000 Å :
- (2) The prolonged duration of the exposure which is required :
- (3) The liability of the salt being separated out, both at the upper and at the lower electrode, in consequence of the prolonged transmission of sparks, a result which may become a serious source of errors in quantitative analyses.

At the outset we made experiments with the glass tube liquid spark-gap shown in fig. 12, in order to ascertain whether the intensities of spectrum-lines of different metals in solution could be quantitatively reproduced for a given solution. It was found that this was the case only when during the passage of the sparks the solution was continuously supplemented in sufficient quantities with the aid of an appropriately set dropping device so that the spark may not by any chance pass over to the boundary of the glass, where salt is very liable to be separated out. The extent to which conditions change when the spark, instead of passing over to solutions, leaps over to suspensions and precipitates of salts is shown by the following experiment.

A mixture of lead chloride and tin chloride ($\text{Pb} : \text{Sn} = 1 : 1$) in a moist condition was placed upon a lower cadmium electrode, which was enveloped by a glass tube extending 4 mm. above it so as to prevent the salts from falling off. The spectrum then showed the ratio of the lead to the tin to be about 1 : 20 instead of 1 : 1 as it was in the spark-gap above a solution.

When the other larger spark-gap is employed all these sources of error vanish. In particular, the required time of exposure reduces to a few seconds ; also the band-spectrum becomes less pronounced. On the other hand, the resistance spark-gap obviously admits of many

spectrum-lines of the dissolved metals (especially absorption lines) being observed within the short-wave regions of the spectrum in somewhat lower concentrations than is practicable with this second arrangement. Where a special problem presents itself it will therefore be necessary to try out the liquid spark-gap which is best adapted for the purpose.

We have also experimented in order to decide the question as to whether colloidal metal solutions or those of metallic salts are capable of being tested in such spark-gaps. The experiments occasionally succeeded well, but less so in other cases. Obviously it depends upon the size of the particles as to whether during the spraying of the liquid they are torn into the spark-gap and there volatilized. These relations require further investigation since there are many analytical problems (such as the examination of washing water, waste lyes, and such like) which may well be capable of being dealt with in the way here suggested.

We have made experiments in an attempt to obtain *spectra of dry salts* with the aid of the saucer spark-gap apparatus shown in fig. 13 by causing the spark to pass through the salt. No spectra suitable for analysis resulted. The spark passes from the upper electrode through the salt to the other electrode. The small crystals are indeed partly fused and disintegrated but the amount of salt which actually passes into the spark track is evidently too small.

If, on the other hand, an insoluble salt in a finely powdered state is made into an electrically conducting semi-fluid mass with common salt solution, for example, and applied to the saucer spark-gap a very sensitive method is frequently obtainable for identifying the metal in the salt. Thus it has proved practicable by this method to readily obtain the complete spectrum of iron in the water-insoluble sinter of the hot spring of Wiesbaden. We believe that the following consideration may explain this result: As the spark traverses the moist salt it gives rise to a disruptive form of evaporation of the liquid and thereby causes particles of salt powder to be hurled forth, which thereupon volatilize in the spark-gap. That both the spark and the solution are the seat of an extraordinarily high temperature of volatilization and of very high local densities is evidenced by the fact that the Balmer series of hydrogen results in great intensity. Frequently $H\alpha$ and $H\beta$ occur as a band covering a width of about 100 Å with self-reversal of a width of about 50 Å.

A suspension of extremely finely-powdered magnesite in water scarcely shows the otherwise very sensitive basic lines of calcium. Neither does the addition of common salt solution improve matters to any appreciable extent. When, on the other hand, a drop of hydro-

chloric acid was applied to the slurry the complete spectrum of magnesium and calcium resulted forthwith.

We make reference to these experiments because they show that the spark method offers prospects of success when applied to the analysis of other substances apart from metallic electrodes and salt solutions. We draw special attention to these potentialities of the method since in our experience, spark-spectra, wherever obtainable, provide the simplest means of carrying out quantitative analyses of every kind.

(d) THE SPECTROGRAPH

The choice of the spectrograph is likewise governed by the nature and purpose of the investigation.¹

In no case, however, is it advisable to employ grating spectrographs for the purposes of chemical analysis. Quite apart from the complicated nature of an arrangement involving the use of concave gratings, such as alone enter into consideration where ultra-violet spectra are concerned, there is the further defect that the amount of useful light is very deficient owing to the fact that the energy radiated into

¹ We have experimented with different forms of apparatus made by Fuess (Berlin), Zeiss (Jena), and Hilger (London). The quartz spectrographs of Fuess have simple quartz lenses, in consequence of which they are difficult to adjust, and the plate is so deeply curved that it becomes necessary to use special extra thin plates. These are obtainable at a very high price only, and acquire a permanent flexure if allowed to remain for a prolonged period in the dark slide, so that subsequently they do not lie flat on the comparator stage.

In the model for 15×10 -cm. plates it is practicable to work with considerably less curved plates and hence ordinary commercial plates may be employed with it. By suitably adjusting the spectrograph, it becomes practicable to obtain sufficiently well defined spectrograms of the most important region extending from 4000 to 2500 Å, in fact, so sharply defined that the analysis of platinum with respect to iridium, rhodium, palladium, etc. may be satisfactorily carried out. Also a position of lenses and an appropriate inclination of the camera may be found whereby sharp definition results between 3000 and 2200 Å. Whether this may be likewise accomplished with the large model (25×10 -cm. plates) has not yet been ascertained by us from actual tests.

Zeiss makes an apparatus for 18×13 -cm. plates with a quartz-fluorite achromatic lens in the collimator (F 20) and a quartz lens in the camera. In this case the plate is no longer curved, and definition suffices throughout the entire range. It would be better if the light-transmission were a little greater, in which case, however, the price of the apparatus would necessarily rise very considerably.

Hilger's apparatus for 25×10 -cm. plates likewise yields sharply defined spectrograms but, owing to the requisite curvature, the plates may not be too thick.

By way of apparatus with glass equipment we use a ($10 \times 8\frac{1}{2}$ -cm.) Hilger spectrograph and a Fuess (15×5 -cm.) spectrograph. Both are to be recommended, the latter having a large dispersion and a great light-transmitting capacity for the most important region of about 4300 to 3900 Å. The former has a wavelength screw which renders it also available for ocular measurements.

We append these particulars without, however, taking it upon ourselves to recommend the apparatus of any particular firm in favour of that of any other maker. While a well designed and well made apparatus is desirable, an intimate knowledge of the principles of construction of the apparatus which is in use is of greater importance. It is practicable to carry out successful analyses with an inferior apparatus if one knows the potential sources of error and is able to take these into account.

the apparatus is distributed among the direct image, the spectrum symmetrical with the one which is being employed, and spectra of other orders. For qualitative analyses, moreover, gratings are useless in view of the grating ghosts which arise.

The light-transmitting capacity at full aperture should not be less than $F\ 20$, reckoning with the relative aperture of the optical portion of the spectrograph which has the smallest light-transmitting capacity. The dispersion of the quartz apparatus should be at least $80\ \text{\AA}$ per mm. at $3900\ \text{\AA}$, 55 at $3500\ \text{\AA}$, 30 at $3000\ \text{\AA}$, and $17\ \text{\AA}$ per mm. at $2500\ \text{\AA}$.

With a dispersion of this magnitude the whole of the analyses described in this book may be carried out, including those of platinum, palladium, iridium, etc. with their many lined spectra. For the spectrum analysis of iron with respect to slight admixtures, this degree of dispersion may be slightly deficient.

We now proceed to discuss briefly the general construction of a spectrograph, while for a more complete study of the details we would refer the reader to the available literature.¹ Fig. 14 shows diagrammatically a horizontal section and the course of the rays through the spectrograph.

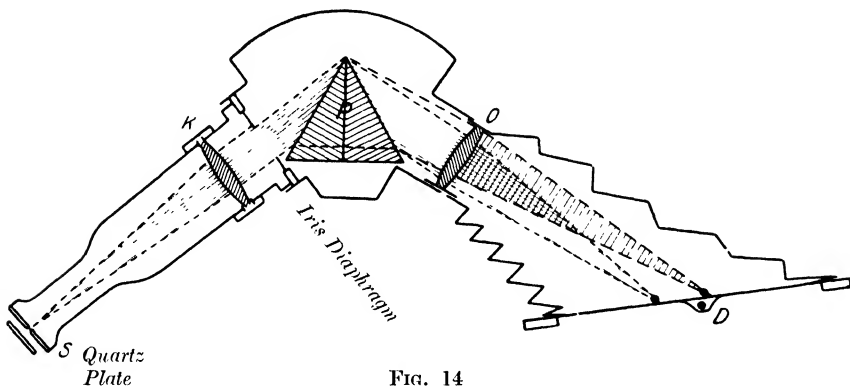


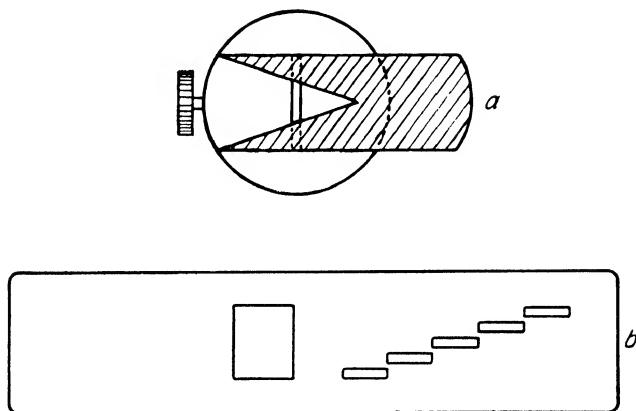
FIG. 14

The slit S should have perfectly parallel jaws of steel with a parallel motion, and these should be lightly held together by a spring. The motion screw should solely draw the jaws apart against the tension of the spring, but in no case should it press the jaws towards one another. It is moreover important that the slit should be at right angles to the axis of the collimator lens and parallel to the refracting edge of the prism and accurately centred. The width of the slit, which is normally read off by the micrometer screw, is best gauged when the slit is exceedingly narrow (approx. $0.04\ \text{mm.}$) by means of the diffraction image,

¹ H. Konen, "Spektroskopie," in his *Handbuch der Arbeitsmethoden der Anorganischen Chemie* II (second part); F. Weigert, *Optische Methoden der Chemie*.

which may be accomplished by looking through the camera upon the prism (while no image of the spark should be allowed to form). Finally, care should be taken to ensure that the inside surfaces of the spectrograph are completely blackened. The slit may be cleaned with a pointed rodlet of wood or aluminium (but on no account should alcohol be used).

The slit has in front of it in a slide-fitting a slit-diaphragm. This has a V-shaped opening and provides a means of varying the length of the slit (fig. 15 *a*). For the purposes of qualitative analysis the diaphragm shown in fig. 15 *b* has proved to be useful. It consists of a set of very *shallow* apertures, through which the spectrum of a specimen taken with the full length of the slit may have successively superimposed upon it the spectra of metals whose presence is anticipated in the specimen (cf. p. 56, fig. 17).



FIGS. 15 *a* and *b*

The collimator lens *K* and camera objective *O* serve the purpose of forming a sharply defined image of the slit upon the plate. The prism exercises a deteriorating influence upon the quality of the optical image. The defects which arise are least in magnitude :

- (1) when the rays passing through the prism are parallel, and when
- (2) the course of the rays through the prism is symmetrical. Both conditions should be satisfied as nearly as practicable, whilst they cannot be strictly fulfilled.

The *collimator lens* serves to render parallel the rays which proceed from the illuminated slit. Within the visible spectrum this is accomplished by means of a crown-flint achromatic lens. Where, however, in the case of a quartz spectrograph it takes the form of a simple quartz lens focusing can be effected for one particular wavelength only with accuracy. In superior forms of apparatus for ultra-violet it is

therefore usual to employ achromatic lenses made up of quartz and fluorite or quartz and rocksalt.

The symmetrical path of the rays in the prism P establishes the important condition that in this case the deviation of the rays is a minimum. Naturally this may be accomplished for a single wavelength only, which should preferably occupy a mean position in the region of the spectrum under investigation. In quartz-spectrographs the prism should always consist of two components of left-and-right rotation quartz (Cornu prism with a refracting angle of usually 60°). In glass spectrographs, compound prisms require to be used in order to obtain a sufficiently pronounced dispersion in the yellow and red regions.

The camera lens O forms an image of the slit upon the photographic plate. It need not necessarily be achromatic, in that the chromatic deviations may be sufficiently compensated by the simple procedure of setting the photographic plate at an angle. On the other hand, it is all the more important that it should be of an exceptionally high degree of spherical correction and freedom from zonal errors.

The dark slide with the plate therein rests in a frame, which is capable of being slewed (about D) and which has a rack or other motion device for displacing the dark slide so that several spectrograms may successively be taken on one plate. Zeiss and Hilger furnish a wavelength scale attachment with instructions for directly printing it upon the plate. This is very convenient for obtaining a rapid orientation over the regions of the spectrum and for finding the lines required in the quantitative analysis, but naturally it is not, neither is it intended to be, accurate enough for measuring the wavelengths of spectrum-lines with the degree of precision frequently needed for qualitative analysis.

The dispersion of the spectrographs is not absolutely invariable at different periods. This should be borne in mind more especially when making comparisons of spectrographic analyses with standard spectrograms taken at other times. These variations in the dispersion arise from dimensional changes in the metal parts due to thermal influences and in the case of glass spectrographs from the high thermal coefficients of dispersion of the heavier kinds of glass.

The spectrographs are supplied by their makers in a permanently adjusted condition. Nevertheless it becomes frequently necessary to re-adjust the instruments. It is inherently impossible to obtain the spectrum equally sharply defined over its entire range, excepting where very much more costly apparatus is employed. In the majority of cases the maximum degree of sharpness is confined to a certain region of the spectrum. It may happen that this maximum of definition

is required in another region of the spectrum. Where the collimator is equipped with an achromatic lens this may be quickly obtained by slewing the dark slide about D (see fig. 14) and displacing the camera lens by small amounts and each time taking a spectrogram. A few trial plates taken in this way soon establish the required adjustment.

Where the collimator lens is not achromatic the adjustment may be a somewhat laborious business. Of the three variables, viz. the distance from the slit to the collimator, that of the camera lens to the plate, and the inclination of the plate, two should be always kept constant while the third is being varied, and this step-by-step procedure should be continued till the best conditions of adjustment are obtained.

(e) ILLUMINATION AND OPERATION OF THE ADJUSTED SPECTROGRAPH

The illumination to the spectrograph may be furnished either by the spark being placed directly in front of the slit or by forming upon the slit an image of the source of light with the aid of a lens. The choice of one or the other arrangement depends upon the purpose which the spectrograms are to serve and upon a variety of incidental circumstances. The formation of an image by a lens is resorted to when a wide beam of light is required and as a means of taking advantage of the full aperture. This is desirable in particular with sparks of small intensity or where, for any reason, very short exposures are to be given. An image of the source of light should also be formed where it is required to know the series type of the lines and the position of their centres of emission respectively within the source of light, and, finally, when it is required to establish differences between the upper and lower electrode. This is practicable by reason of the stigmatic formation of the image of the slit in a prism spectrograph. Finally, this arrangement should be chosen where for technical reasons one is forced to keep the source of light at a great distance from the spectrograph.

In every case care should be taken to ensure that the centre of the spark may be accurately in the optic axis. To ensure this the dark slide should be removed and the slit set wide and, by looking through the spectrograph, the position of the spark noted, which should be accurately in the centre of the collimator lens. The position of the image-forming lens should be such that the diaphragm may be completely filled with light. Incidentally it is an advantage to form a magnified image in order that the setting with respect to the slit may be obtained with greater ease and certainty, and so that the slit may receive light throughout its entire height, even though theoretically nothing is gained thereby in the matter of light.

If a blurred image of the source of light be formed on the slit by

setting it out of focus the arrangement will approximate to that without a lens. In this case only a very thin cone of light depending upon the size and distance of the spark will enter the collimator tube. In a measure, however, as the slit is narrowed the cone widens and the collimator lens receives more and more light. On the right and left diffraction images of higher orders arise. *According to the desired width of the slit the iris-diaphragm should be opened until it just includes to its full extent the principal maximum, while stopping off the secondary maxima.* In spectrographs of small light-transmitting capacity the principal maximum often covers the unstopped collimator lens.

Where the investigation is in the nature of a *quantitative analysis* the most favourable conditions may unquestionably be established by working without forming an optical image of the spark. Quite apart from the fact that illumination by the formation of an image renders it far more difficult to compare spectrum-lines owing to the uneven distribution of the intensity along the path of the spark, the relative intensities within the spectrum are subjected to small variations in the image according as it magnifies or diminishes the spark or occupies a symmetrical or dissymmetrical position. Small changes in the passage of the spark suffice to cause these variations. The absolute method of homologous pairs of lines (p. 67), while not fundamentally affected thereby since the centres of emission of the homologous lines are isotopically situated, the optical method of reproducing the conditions of discharge (p. 71, fig. 23) fails since a spark-line is not in any circumstances comparable with an arc-line. Spectra taken without a spark-image may be recognized by the perfectly uniform distribution of the intensity throughout the entire height of the individual lines and bands

For the protection of the slit from injury by chips from the spark, and especially from sprayed fluid from the solution electrode, a small quartz plate should be placed in front of it.

(f) EVALUATION OF THE SPECTROGRAMS

We assume that there is no need in this book to enter into a discussion of the photographic procedure. It may be sufficient to mention that for work within the blue, violet, and ultra-violet regions of the spectrum the use of extra-rapid plates is to be preferred. For spectrograms in the visible regions use should be made of the commercial isochromatic or sensitized plates, such as Hauff's panchromatic plates (for green), Ilford Iso-Zenith (for yellow-red), Perutz Brown Seal (for yellow to green), Eastman-Kodak "extreme red sensitive" (long wave red, *e.g.* potassium basic lines). The necessity of sensitizing by the operator has thereby been well-nigh eliminated.

Two modes of evaluating the plates enter into consideration, viz. the measurement of the wavelength of the spectrum-lines for their identification as unmistakably characteristic and indicative of a chemical element (by way of qualitative analysis), the other mode being the photometric evaluation (for the purposes of quantitative analysis). The developed plate may be viewed with a lens magnifying 5 to 10 times.¹ It is likewise convenient and useful to project a magnified image upon a screen. The image may then be measured with an ordinary rule within small regions.

For the exact *measurement of the wavelengths* of the lines it will be necessary to use a reading microscope or a comparator, such as are produced by various makers in more or less elaborate forms. In most cases a comparator may be dispensed with, and indeed it is sufficient in most cases to be able to measure lengths of 2 to 3 cm. on a plate with a degree of accuracy of 0.01 mm. For the use of works laboratories we would recommend double eyepieces, with the aid of which two observers are enabled to view a plate jointly. This greatly facilitates the mutual discussion of doubtful lines. Double comparators are likewise very convenient in that they admit of a direct comparison being made of a test spectrogram with a standard or comparison spectrogram.

Relative photometry, as applied by us to our methods of quantitative analyses (see chapter V), consists merely in the visual estimation of like intensities of neighbouring spectrum-lines. A well corrected lens magnifying 5 to 10 times is required and quite sufficient for this purpose. In this case it is likewise advantageous to project a moderately magnified negative upon a screen. Very small departures from equality in the intensities are then readily recognized (*i.e.* with rested, not with dazzled eyes).

(g) PHOTOMETERS

The direct method of spectrophotometry is applied in rare cases only since the visible region of the spectrum contains a negligibly small number of lines which are adapted for the purposes of chemical analysis. These occasions present themselves, amongst other investigations, in the case of the flame spectra of the alkaline earths, where it is practicable to establish a direct photometric comparison of a flame impregnated with standard solutions and an exactly similar flame into which the solution to be analyzed is sprayed in a precisely like manner.² For

¹ For this purpose a small wooden or iron stand should be made of a length of 20 cm. upon which the plate should be laid. The latter should be illuminated from below with a mirror, while the magnifier should be held in a mount capable of sliding along the plate.

² H. Lundgårdh, *Die quantitative Spektralanalyse der Elemente*. Jena: Gustav Fischer, 1929.

this purpose a spectrophotometer is used, one slit (or half slit) of which should be illuminated by one flame, the other slit (or half slit) by the other flame, and the resulting intensities of directly superimposed contiguous parts of the spectrum compared. The photometric apparatus (usually a Nicol arrangement) admits in these cases of the spectrum-lines being set to equality of intensity, and from the position of the Nicols the ratio of the intensities may be determined.

In the majority of cases the aim of the photometric evaluation is to determine the intensity of the selected spectrum-lines from the intensity of the blackening produced by them on the photographic plate.

The photometric evaluation of the plates bearing these spectrograms does not involve fundamental difficulties in any cases where it is a matter of accurately establishing the equality of two spectrum-lines or small departures from equality (cf. Chapters V and VI). For this purpose, if it be desired to refine the personally visual mode of estimation, a large number of photometers are supplied by various makers. Some of these are based upon the principle originated by P. P. Koch, others upon that evolved by Moll. The former employs photo-electric cells,¹ the latter thermo-couples² as the basic device for measuring the intensity of the source of light transmitted through the blackened portion of the plate (*i.e.* through the photograph of the spectrum-line).

We shall content ourselves with a brief indication of the principle of these photometers. They consist essentially of a source of light L (filament lamp, Nernst filament, fig. 16), which illuminates through a condenser L_1 a slit Sp . A reduced image of the latter is formed (by a microscope arrangement L_2) upon the plate P which is to be measured

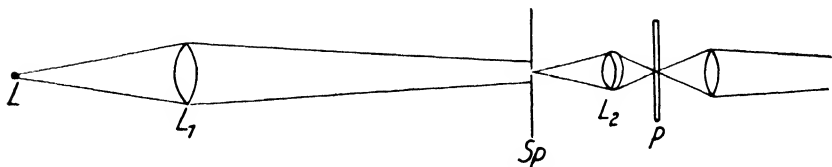


FIG. 16

photometrically. The transmitted light is projected by means of L_3 upon the photo-electric cell. A galvanometer or an electrometer is employed to measure the photo-electric current which is generated, both when the light passes through a portion of the plate at the side of the spectrum-line and when it passes through the blackened spectrum-line.

¹ *e.g.* Koch-Goos's photometer, the Zeiss photometer, the Rosenberg photometer made by the Askania Works.

² The Moll photometer made by the Messrs. Kipp & Zonen, Delft (Holland), and the recording photometer of the Cambridge Scientific Instrument Company, England.

In the place of the cell a thermocouple with a galvanometer may be employed for this purpose. In many photometers the course of the rays also includes a so-called neutral-tint wedge, which should be clear at its thin end and almost opaque at the thick end. The wedge is movable in the direction of its blackening gradient and should be so set that in all measurements the galvanometer gives the same deflection. If, accordingly, first a light and then a dark portion of the plate *P* be illuminated, a measure of the density of the blackening is furnished by the amount of displacement of the wedge required to compensate the change occasioned by the radiation transmitted through *P*. (Method of Halban, Rosenberg.)

In many cases a simple visual photometer designed on the principle devised by Hartmann will suffice, especially where it is practicable to employ sufficiently broad spectrum-lines (for further particulars see Chapter VI).

CHAPTER IV

QUALITATIVE ANALYSIS

In the introductory chapters we have occupied ourselves with the fundamentals of a system of qualitative chemical analysis by the interpretation of spectrograms. We shall now proceed to deal only with the practical application of these principles. At the outset it may not be superfluous to point out that the qualitative aspect of the analysis frequently presents far greater difficulties and makes far greater demands upon the care and circumspection of the operator than the quantitative side of the method, which we shall discuss later.

It is also well to realize at the outset that there are cases where the resources of the qualitative method are still an unknown factor as well as cases where they are as yet very limited. This includes in particular the identification of the non-metallic elements. We shall accordingly confine ourselves to metallic elements.

If nevertheless we advocate the practical use of the qualitative method, it is in virtue of very surprising experiences which we have been able to record in the course of the last few years in connection with specimens submitted to us by technical establishments for the purpose of trying out certain spectro-analytical methods.

We have by these experiences secured evidence of the existence of *numerous* cases in which the qualitative analysis by the spectrum is capable of detecting the presence of wholly unexpected impurities which could not possibly have been identified by chemical analysis. (Thus in samples of zinc we were able to detect minute quantities of *gallium*, on another occasion the element *scandium* in a sample of silver).

It appears also that qualitative analysis cannot be dispensed with in mineralogical investigations. By way of an example we may mention the experiments of H. Fesefeldt,¹ which will be more fully dealt with elsewhere, and the object of which was to demonstrate the presence of beryllium in minerals of the most varied composition, or the older experiments of G. Eberhard² on the detection of scandium, and those made by Wild³ in an investigation of the colouring constituents of gems.

Another technical problem for qualitative analysis which we may

¹ H. Fesefeldt, Zts. f. physikal. Chemie. A. 140 (1929), 254.

² G. Eberhard, Sitzber. Preuss. Akad. Wiss. 23 (1908), 851.

³ Wild. Neue Jahrbücher für Mineralogie etc. Suppl. vol. LV, Sect. A. (1927) 488

mention is the *investigation of the composition of very small specimens* which are also to be subjected to other tests including, say, metallographic observations. Such cases also occur in connection with the explanation of faults present in a given material, for instance in support of claims, as analytical evidence in a court of arbitration, or as a means of verifying the composition of the products of competitive manufacturers. The choice of the spectro-analytical method in such cases may be determined by the condition that the specimen shall *remain intact* or that the test shall be capable of being applied indefinitely often by different enquirers, or, finally, that the spectrogram may serve as important documentary evidence in litigations. In the majority of such cases the evidence furnished by the spectro-analytical document is irrefutably convincing and can at all times be verified, whereas a chemical analysis derived from a single minute sample is invariably full of pitfalls and dominated by the personal factor. We may instance in this connection an actual case concerning a claim respecting the delivery of a metal which is produced by a number of establishments by different processes. After the chemical method had failed, it proved practicable to identify accurately by the spectro-analytical method the source whence the metal had been derived from the demonstrable presence of very minute impurities which by their different natures were characteristic of the methods of production adopted in the two works in question. Hull and Steel likewise have recently recommended the spectro-analytical method,¹ for rapidly identifying the origin of a given sample of aluminium and the nature of an aluminium alloy—duraluminium, silumin, etc. Finally, it may be pointed out that for the purpose of subsequent verification by the spectrographic method, only small samples need be retained, and that the spectroscopic method provides an expeditious means of separating accidental from uniformly distributed impurities. (This aspect will be fully dealt with in Chapter VII on “local analysis.”)

The limiting quantities which are capable of detection and identification are extraordinarily small. The absolute order of magnitude of these limiting quantities obviously varies widely with the method of luminous excitation, also, in the case of solutions, with the nature of the kation and anion, in that of solid electrodes with the vapour pressure of the primary substance (see p. 25). Of the available data we may give those of Walter, Hartley and Moss,² who show that quantities of 7.5×10^{-7} grm. of cobalt or 2×10^{-9} grm. of manganese are capable of spectro-analytical identification in the spark.

¹ F. A. HULL and J. J. STEEL, Proc. Am. Soc. for Testing Mat. 1927, Part II (quoted by Twyman, Zeitschr. d. Ver. D. Ing. No. 6, 1929, 199).

² HARTLEY and MOSS. Proc. Roy. Soc. A. 87 (1912), 38.

The *complete qualitative analysis of a material* is more difficult than the quantitative determination of an added *known* component for this reason, apart from others, that in every initial analysis entered upon without any knowledge of the composition of the substance, and above all without any knowledge of elements which are present in small traces only, a good deal of work has to be gone through which in the quantitative application of the method has been accomplished once and for all (as will be instanced by the cases dealt with in Chapter V).

We will now consider the problem in its most general aspect. Let it be required to identify all the metals present in a specimen presenting a metallic character and regarding the composition of which no data whatever are known. The first spectrogram, in many cases even a visual spectroscopic observation within the visual region of the spectrum, at once discloses the principal component or components of the specimen. For the purpose of simplifying our description it may be assumed that one particular element occurs in predominant proportion and that therefore all other kinds of atoms which are present occur only as admixtures or impurities in very small proportions. Of this primary substance (*P*) a pure specimen¹ shall be supposed to be available (respecting the estimate of the true purity of this specimen or the necessary measures to be adopted in the event of its deficiency see subsequent paragraphs). These additions, without reference to their nature, shall be denoted by the letter *A*.

We shall now describe the procedure by which we have found it practicable to achieve reliable results with the greatest expedition.

On a first plate several spectrograms of the specimen should be taken, the specimen being one which has not been subjected to any previous spark discharges ("first sparks"). According to the nature of the specimen or the proposed problem either the existing surface or a fresh fracture or cut surface should be employed. A fracture in this case is to be preferred in order that no impurities (such as iron) may be introduced into the specimen by the cutting. The time chosen for the first exposure should be so short that the available apparatus just brings out all the heavier lines of the spectrum in accordance with the operator's experience of his equipment. With the succeeding spectrograms the time of exposure should be increased, taking care, however, that the specimen may not become hot. If the specimen be of a kind that the electrode heats easily, as may happen when it has fine points or where it is in the form of a thin wire, the exposure should be interrupted at short intervals. During these exposures the electrodes

¹ Respecting the significance of these first spectrograms in relation to the identification of "external impurities" see below (p. 63).

should not be touched so as to avoid contamination (especially with calcium or magnesium). Neither should the specimen be etched with an acid before taking the spectrogram.

Next, on a second plate a series of spectra of the specimen should be photographed with the dark slide set to positions 1, 3, 5, etc. Without making the slightest change in the arrangement, the spectra of electrodes of the purest available specimen of the primary substance should be photographed at very slightly varied times of exposure upon the places 2, 4, 6, etc. On the developed plate we now proceed to seek out the pair of spectra where the corresponding *P*-lines are most nearly of equal intensity. Now the entire plate should be examined under the comparator while continuously displacing the slide-carriage and all those places marked on the plate where differences present themselves in the two spectrograms. Since the *A*-lines are of low intensity when the concentrations of *A* are small, extreme care should be bestowed upon the detection of minute differences.

Differences in the definition of corresponding spectrum-lines of *P* should be likewise taken into account since an *A*-line may possibly be so close to a *P*-line that they do not appear separated in the spectrogram.

We now proceed to measure the wavelengths of the lines which occur in the spectrum of the specimen but are absent in the "pure" spectrum. To this end we identify the heavy and easily recognizable *P*-lines in close proximity to the lines in question with the aid of an atlas of spectra and estimate or determine by means of a comparator the wavelengths of these lines by interpolation.

It is incidentally exceedingly useful to prepare for permanent use a few plates showing a wealth of identified lines ("dispersion plates"). For this purpose the spectrum of platinum with its many lines is well adapted, being obtainable in great purity. The following procedure

is likewise simple. Upon the same part of the plate the spectra of Pb, Sn, Bi and Au should be photographed one superimposed upon the other through a successively shortened slit (as indicated in the diagram in fig. 17), and the appropriate wavelength appended to each line. The Ca and Mg-lines, which are due to atmospheric dust and which are always present more or less prominently, should be specially noted.

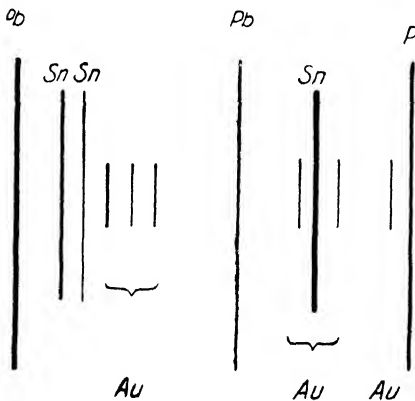


Fig. 17

The two plates, *i.e.* the dispersion plate and the analysis plate, should now be so placed upon one another that the Ca and Mg-lines coincide. Looking through the plates, the wavelengths may now be determined by comparison. It should be noted that the dispersion of a spectrograph depends upon the temperature, in consequence of which small variations may obtain in the distances between the lines in spectrograms taken at different times.

The wavelength of the *A*-line in the spectrum of the specimen having been determined more or less exactly, Kayser's tables of the principal lines of the elements ¹ provide a means of identifying all those metals which furnish a strong line in close proximity to the wavelength which has been determined. Where one and the same element is suspected to be the source of emission of many or the whole of the lines foreign to the primary or *P*-spectrum the presence of that element is at least probable. With the aid of tables, such, for instance, as F. Löwe,² F. Twyman,³ and D. M. Smith⁴ have compiled, the "sensitive" or "ultimate" lines of the suspected element may readily be found. Where the supposition is well founded, these lines should appear on the spectrograms of the specimen.

Should the correspondence of the lines not yet be completely established several spectrograms of the suspected element should be made on another plate with different times of exposure, and, in addition, a new spectrum of the given test specimen should be photographed. On another spectrum of the specimen a superimposed spectrum of the suspected element should be photographed through a shortened slit without making the slightest change in the arrangement of the apparatus. With the aid of this photograph it will now be practicable to establish the exact intensity and the coincidence of the debatable lines and, in addition, the conformity of the intensities with the spectrograms of the suspected *A* metal furnishes a measure of assurance as to the accuracy of the supposition.

In the event of only one or few admixture lines being found, or where greater certainty is desired, a further criterion may be brought to bear on the test. It consists in varying the conditions of discharge when taking the spectrum of the specimen, especially as regards the self-induction. Thus, the character of the admixture line, as to whether it is an arc-line or a spark-line, may be recognized and be made to serve as a valuable suggestion.

¹ H. KAYSER. Tabellen der Hauptlinien der Elemente, publ. by Hirzel, Leipzig, 1927.

² F. LÖWE, Atlas der letzten Linien der wichtigsten Elemente, publ. by Steinkopff, Dresden, 1928.

³ F. TWYMAN and D. M. SMITH, Wavelength Tables for Spectrum Analysis, publ. by Adam Hilger, Ltd., London, 2nd Edition, 1931.

⁴ D. M. SMITH, Visual Lines for Spectrum Analysis, publ. by Adam Hilger, Ltd.,

As a rule this mode of carrying out the qualitative analysis does not involve any further difficulties. Frequently, however, there are available neither suitable pieces of *P*, *i.e.* the chemically pure primary substance, nor of the admixed substance *A*.

In these cases, too, a remedy is at hand. Where a specimen of the primary substance of guaranteed chemical purity is not at hand, spectrograms should be taken of specimens of *P* of the highest degree of purity which are obtainable, preferably derived from different sources. It will then be practicable to say with a fair degree of certainty which of the lines, including the faintest of them, appertain to the primary substance and which are to be ascribed to the admixture, for the latter, even if they should happen to be qualitatively alike in all *P*-specimens, are not likely to be present in exactly equal proportions. The lines appertaining to the impurities will therefore be recognized by their variable intensities in different specimens.

Where even *P*-specimens of this degree of purity are not available and especially where no pure *A*-substance is available (or at least a material which contains *A* with certainty) there is nothing left but to measure the spectrogram at all suspected places with the aid of the comparator, to determine the wavelengths of the lines in question as accurately as possible, and, *having due regard to the attained degree of accuracy*, identify the principal lines of the elements by Kayser's table of the principal lines. Where one or several spectrum-lines point to a certain element, the *basic lines* of the supposed element, which may be taken from these tables, should under all circumstances occur as the lines of greatest intensity. Unless this is the case the identification of the element cannot be accepted as unquestionable. When estimating the intensity, the question as to whether lines of impurities may possibly coincide with weak lines of the primary substance should be tested with the utmost care.

An analysis of this kind involving the exact measurement of wavelengths is certainly not easy, and it is equally certain that it cannot be carried out without the utmost care and precision. On the other hand, it should not be overlooked that this method yields results which cannot be obtained by any other method. We know from experience that the trouble which it involves may bring its full reward. Two instances may suffice to show this. In one it disclosed quite unexpected traces of scandium in a sample of silver, in the other it provided an equally surprising proof of the presence of gallium in a specimen of zinc containing cadmium. In the latter case, however, very exact measurements were needed to complete the analysis. Gallium was identified by the two lines 4172.05 and 4033.01 Å on spectrograms taken with a Fuess glass spectrograph (dispersion 13 Å per mm.) The line 4033.01 is

situated close to a pronounced manganese line 4033·17. Yet the presence of manganese was readily eliminated by the absence of other intense lines, especially the neighbouring line 4030·76.

Where it is a matter of analysing a quantity of substance which is too small for chemical analysis, while at the same time it is *not required to preserve the specimen intact*, many different ways offer themselves of arriving at the desired goal by a combination of chemical methods of analysis and the spectrographic mode of examination. We shall confine ourselves here to a few suggestions regarding the procedure which in our experience may yield successful results.

A first course which may be adopted is to remove by precipitation certain elements from a solution of the specimen. This course is to be recommended where the specimen contains a large number of elements, in which case the spectrum may contain an excessive number of lines with frequently recurring coincidences of spectrum-lines due to different elements. In this case an attempt may be made to eliminate by precipitation, *e.g.* the primary substance, after which the residual solution may either be examined directly by sparking the solution, or the solution may be concentrated before taking its spectrogram. A particularly important means of concentration has been found by us to be the method of electrolytic deposition of metallic ions upon a suitable electrode, such as of very pure gold or pure platinum. Where the electrode which receives the deposit is sufficiently small the whole metal content of the solution concentrates upon the small surface. The *first* sparks passing over to this electrode will then in the main only volatilize the coating which is to be analysed. The opposite electrode should likewise be gold or platinum, both on account of their small vapour pressure and by reason of the great purity in which these two elements are obtainable. On the other hand, an element may be chosen the spectrum of which is lacking in lines, such as purest cadmium (assuming this to have been tested spectro-analytically).

Respecting the absolute quantities of substances which in the form of electrolytic deposits are capable of being identified by spectrum analysis we are able to refer to quantitative experiments conducted by E. Bayle and L. Amy.¹ In these experiments iron and copper were deposited electrolytically from the given solutions upon carbon electrodes. In this way 10^{-7} grm. of iron per gramme of citric acid and 5×10^{-7} grm. copper per gramme of zinc were capable of being analysed qualitatively.

It is necessary in the application of the method of chemical precipitation to examine also the precipitate by spectrum analysis; for it may well happen that particular importance attaches to the detection

¹ E. BAYLE and L. AMY. Compt. rend. 185. (1927), 268.

of an element which, being closely allied to the primary substance, may have been precipitated jointly with it. The best course is to re-dissolve the precipitates for spectrum analysis in the spark from the solution. Fine-grained salts can also be spectrographically examined by the filter paper method described on p. 39. This applies in particular to spongy precipitates of metallic compounds which are thereby volatilized in the spark-gap.

In the discussion of the method we have so far confined our attention to the analysis by the *spark-spectrum*. *Where the specimen is required to remain intact the only method which is applicable is furnished by the luminous excitation in the spark-gap.* In adopting this method one foregoes at the outset the possibility of detecting by a sensitive method many of the elements which may be no less important than those of the metallic admixtures. In this category we may name in particular arsenic, sulphur, selenium, tellurium in heavy metals. Obviously these elements, being very volatile, escape from the surface of the electrodes and from the path of the sparks before they can be rendered luminous.¹

Their identification, however, is practicable if their excitation be induced in the electric arc; but the limits of concentration for their detection in the arc are not yet known.

For this purpose small fragments of the specimen to be analysed, preferably even powdered, should be placed in the hollow of the lower electrode of a carbon arc. The carbons used must be *very pure* and should preferably be soaked in hot acid for a long time. Before every experiment they should be spectroscopically examined.

The employment of the spark is not confined to metallic specimens. On the contrary, solutions and likewise precipitates, salts, emulsions and the like may under suitable modifications of the arrangement of the spark-gap be examined in this way and subjected to very sensitive quantitative analysis. Solutions of salts should be acidulated, preferably with nitric acid. Hydrochloric acid is likewise adapted for this purpose, but sulphuric acid less so. We shall revert to this more fully elsewhere. The limits within which it is practicable to detect and identify an element qualitatively are not susceptible of a ready statement. There are cases in which the sensitivity is little short of enormous. Thus, bismuth can be easily detected in lead when present in atomic percentage of considerably less than 10^{-4} . In solutions the limit is generally in the neighbourhood of 10^{-2} to 10^{-3} atomic per cent. per gramme of solution.

In many cases where *heavy metals* are to be analysed a particularly

¹ From more recent experiments it seems possible to detect the presence of arsenic in a highly condensed spark.

convenient and extremely sensitive method of qualitatively analysing traces of freely volatilizable admixtures can be applied. By this method, after taking a spectrogram of the specimen under standard conditions, a second spectrogram is taken, but in this case the ends of the electrodes are brought to incandescence or to the fusion of the tip by greatly increasing the stream of sparks. In the event of the specimen containing metals with a high vapour pressure, its spectrum-lines will be intensified by this procedure in that these *A*-atoms are made to diffuse from a deeper stratum ("analysis by heating"). Incidentally it should be taken into consideration that the discharge in this procedure exhibits an arc-like character and that consequently the spark-lines gain far less in intensity. The extent to which the conditions of discharge have changed is shown by the intensity of the spark-lines in relation to that of the arc-lines in the spectrum of the primary substance. By the diminution of the self-induction in the "hot" spectrum these changes may be partly compensated. *If, after the spectrogram obtained by the heating method, a further spectrogram be taken under normal conditions the lines of the A substance will be very much weakened or even disappear.*

We have tried out these "analyses by heating" more especially in connection with lead as an impurity in gold. The danger that the lead might be entirely volatilized out of the gold demanded that the spark-gap should have very little energy impressed upon it. It was found that by intense heating, the lead content in the path of the discharge was very considerably increased. The strength of the primary current to the induction coil was raised to its highest admissible amount of 6-7 amps. while the rate of interruption was raised to 70 per second. The electrodes were made very pointed and narrow and brought within a few millimetres of one another. Under these circumstances the ends of the electrodes, especially that of the upper one, become incandescent and occasionally may even melt. The intensity of the lead-lines undergoes changes during the time that the spark passes in the manner indicated in fig. 18.

The spectra of specimens of gold containing 0.026, 0.003 and 0.0002% of lead were photographed during the time interval *a*—*b* (fig. 18). The spectrum (fig. 19) showed, even when the lead content was as low as 0.0002%, both lead-lines 3684 and 2614 with perceptible intensities, and at the side of them the spectrum exhibited nitrogen bands in extreme intensity. The increase in the intensity

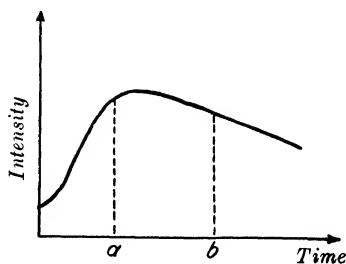


FIG. 18

of the lead-lines may be seen from the tabulated values given below, where the first column shows the true percentage content of lead, the second column shows the concentration of lead which under normal conditions of discharge would yield the equivalent intensity of the lead-lines.

TRUE PERCENTAGE CONTENT	APPARENT PERCENTAGE CONTENT RELATIVELY TO THE GOLD LINES
0.021	3
0.0035	0.6
0.0002	0.02

It will be seen that this heating method extends the limits of the analysis approximately to the second power. It was found that by maintaining the form of the electrodes with moderate precision, as



FIG. 19

FIG. 19. Spectrograms produced by the spark method of heating for the analysis of lead in gold.

The marked lead-lines are distinctly visible at a lead concentration of 0.0002 per cent.

Note the occurrence of the strong bands.

well as the conditions of the discharge and the time intervals, fairly useful quantitative data may be attained (within 50 to 100%).

The uniformity of the intensity of the very pronounced air band spectrum affords a measure of the degree of uniformity with which the specimens have been spectrographed.

We emphasized above the *significance of the possession of extremely pure specimens of the primary substances* contained in the specimens which are to be analysed. This degree of "purity" should be of a

spectroscopic order,¹ that is to say, the spectrum should disclose no other but the primary element.

Such a test of purity is necessary with the substances which are to be employed as standard specimens in conjunction with the quantitative method of analysis which will be described. We may in this place refer to the method described on p. 100, whereby the presence of impurities in "purest" metals supplied by a metallurgical establishment may be determined even quantitatively.

A significant part in qualitative analysis is played by the "*external impurities*." We distinguish between "*external*" and "*internal*" impurities in that the former find their way into the specimen by the manner of storage or its mechanical treatment, or into the electric discharge from the dust of the room, while the latter are inherent in the specimen. In general it may be said that these latter impurities are important enough to be known, whereas the external impurities are liable to prove disturbing. It is important to make a spectroscopic distinction between these impurities and contaminations. Of the external contaminating elements the most notable is calcium from the dust furnished by the walls and ceilings. Among thousands of spectrograms we have encountered very few in which the presence of calcium was not recognizable at a glance. They include, however, also components of crucibles, especially calcium and magnesium, particles of the material by means of which the specimens are prepared, such as the iron of cutting tools, draw-plates, or rolls. These external impurities will accordingly in the majority of cases be confined to the surface of the specimen; and that this is so is borne out by the fact that their presence betrays itself most strongly in the spectrograms in the initial stage of the spark discharge and declines steadily as the discharge proceeds. Their presence may thus be recognized by their gradual disappearance in successive spectrograms. It would nevertheless be a mistake to draw an *unconditional* inference from such a change of intensity in the spectrum-lines to the effect that they are solely evidence of the presence of external impurities. Such a conclusion is particularly dangerous in the case of iron. We have encountered a great many cases in which we concluded at the outset from the changes in the lines of *iron* that the latter derived its presence from the mechanical manipulation of the metal, whereas *subsequently we were able to establish that these*

¹ The expression "spectroscopically pure" is a technical term of purity applied to the rare gases. Purest platinum was hitherto described as "physically pure." It would seem worth while to endeavour to determine a higher degree of purity by application of spectroscopic tests. We would refer to the experiments of W. F. MEGGERS, C. C. KIESS and F. J. STIMSON, Sc. Papers, Bur. of Stand. No. 444, 1922.

Some spectroscopically standardized substances of high purity are supplied by Adam Hilger, Ltd.

lines were due to an uneven distribution of iron within the specimen, for after the iron lines had become fainter and fainter in a series of spectrograms, they suddenly became once more intense. The iron, in fact, occurred in the specimen in the form of small granules (either in the form of the metal or its oxide).¹ From this it follows that occasionally spectroscopic analysis with respect to iron may involve uncertainty. When discussing the "grain boundary effect" (p. 114) we shall instance another case where the successive decline of the intensity of the spectrum-lines of an element may likewise occur in the presence of internal impurities.

The chemical elimination of these external impurities should be applied with care, since it may easily happen that by this procedure "internal" impurities are removed from the surface layer. As the diminution of the thickness which occurs during the production of the spectrum is extremely small it may happen that the strata which are subjected to volatilization thus become chemically purified. Where the specimen is etched with acids several spectrograms may be taken in succession and the internal impurities recognized by the successive intensification of the *A*-lines.

In conclusion, it may be useful to append a few words regarding the "*atmospheric lines*," which arise because every spark, besides bringing about the excitation of the atoms of the metal or their ions also induces the luminosity of the gases of the air.

The lines having an atmospheric character do not exhibit any decrease in their intensities and frequently are liable to be mistaken as indicative of the presence of genuine admixtures, since in specimens of one and the same material they occur under like external conditions of discharge again and again and often with but very slightly varying intensities.

When the nature or size of the discharge surfaces of the electrodes are not uniform variations likewise occur in the rate and quality of the spark passing between them. At the beginning of every discharge, atmospheric spectra are mainly those which are induced first, these being succeeded by the spectra of the metallic vapours which have been evolved in the meantime. Hence, where discontinuities in the spark discharges are very pronounced these deceptive atmospheric lines increase proportionately in intensity. However, this very inconstancy is a characteristic feature of this species of lines and therefore at the outset serves as a warning.

¹ Actually it is often practicable to eliminate iron from "purest" metals in the molten state by allowing them to cool on the pole of an electromagnet, the particles of iron being thereby drawn downwards.

CHAPTER V

THE METHODS OF QUANTITATIVE ANALYSIS

The aim of quantitative analysis is to determine how many out of a hundred atoms of the specimen are composed of the primary substance *P*, and how many of the respective admixtures $A_1, A_2 \dots$, in other words to ascertain the atomic concentration of the *A*-elements. The practical realization of such analysis with the aid of spectrographic methods is based upon the principles expounded in Chapter II, and supported by an account of experimental tests.

(a) THE QUESTION OF THE PRACTICABILITY OF AN ABSOLUTE ANALYSIS BY INTENSITY MEASUREMENTS

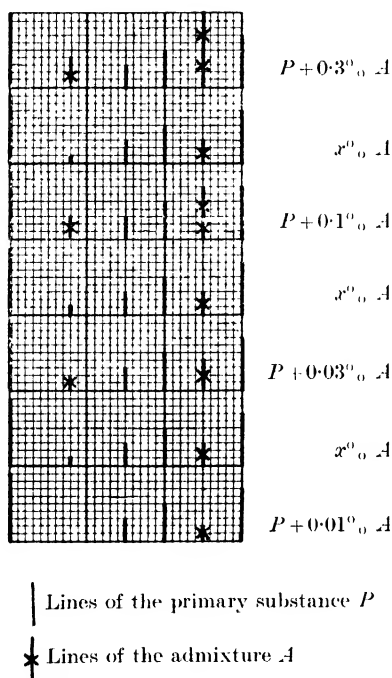
It may be useful at the outset to briefly review the facts which negative the practicability of a direct analysis either from the absolute blackening of the *A*-lines of the spectrum or from the number of the *A*-lines appearing in the spectrum of the specimen.

The photographic *blackening* is for a multiplicity of reasons no measure of the intensity of emission. It is as much dependent upon the type of the spark discharge as it is dominated by the construction and mode of illumination of the spectrum apparatus, the properties of the photographic plate, and the time of exposure. The first named factor includes also the influence of the material of the primary substance of the electrodes and the blackening of the photographic background by bands. — The *number* of spectrum-lines of the *A* element which are still to be seen at a certain *A*-concentration is governed by the like conditions, while the order in which they disappear with diminishing *A*-concentrations is very markedly affected by the nature of the substance of the electrodes. Such absolute intensity methods of analysis may indeed be applicable to certain series of *like* investigations in which the procedure is purely repetitive and conducted under very stringent precautions,¹ but any attempt to generalize them is out of the question. Further analyses performed at different times are not directly comparable with one another.

¹ e.g. H. FESEFELDT, Zeits. f. physikal. Chemie. Sect. A. 140, 1929, 254.

(b) THE METHOD OF COMPARISON SPECTRA

Suppose it be required to determine the percentage content x in an association of two elements of the composition $P + x\% A$. It shall be assumed that a large number of chemically analysed electrodes of the compositions $P + a, b, c \dots \% A$ are available. This being the case, a series of spectrograms are taken of these standard specimens in the order $a, b, c \dots$, and by an appropriate displacement of the dark slide, it should be so arranged that between two successive spectrograms there



Lengths of lines \equiv intensities of lines

FIG. 20.

may be space for the subsequent exposure of a spectrogram of $P + x\% A$. Throughout this procedure the conditions of discharge and exposure should be kept as constant as possible. Then that *pair of spectra* of the standard substance and the unknown specimen should be sought in which the P -lines appear equal in intensity and the A -lines nearest to equality, interpolating where necessary or possible between two successive spectrograms. In fig. 20 part of such a series of spectrograms is represented diagrammatically. The result of the experiment would be to show that x lies between 0.03 and 0.01%.

The accuracy of the results increases with the degree of *equality of intensity in the corresponding lines of the primary substance* and with the smallness of the steps $a - b - c - \dots$ of the standard substances.

This is the simplest and best method of applying the *analysis by identity* and that *by the limit of concentration*. *Analysis by identity* embraces those cases where it is desired to verify whether an alloy has exactly the prescribed composition $P + n\% A$. The method of *analysis by the limit of concentration* is applicable, for instance, where it is required to know whether a prescribed degree of purity of the primary substance has been reached (or exceeded, as the case may be).

In many cases which we have tested (*e.g.* from 1—0.001% Pb in Au, 5—0.001% Cu in Mg or Al, 1—0.0001% Bi in Pb) we have been able to confirm the great precision of the analysis by the method of equal intensities. This method may also be further refined by the application of photometric measurements (see Chapter VI).

(c) THE ABSOLUTE METHOD OF HOMOLOGOUS PAIRS OF LINES

The visual estimation of the degree of blackening of a spectrum-line, such as may be obtained with the aid of a magnifier, depends upon the strength with which this spectrum-line stands out from its background. Where this spectrum-line appertains to an element A , the quantity of which present in the primary substance P of the electrode is to be determined, *a measure of its degree of blackening is furnished by comparison with the blackening of a spectrum-line of the primary substance P situated in its proximity and on a like background.*

This then represents the chemical spectrum analysis in its most direct form, i.e. the required ratio of the quantities of A and P is determined from the ratio of the intensities of the spectrum-lines of A and P .

If in any special case an A -line resulting at a concentration of $p\% A$ in P should prove to exhibit the same intensity of blackening as a P -line the conformity of the blackening persists when the time of exposure is varied, even when the blackening belongs to the order of over-exposure or under-exposure : assuming that the condition of equal intensity was *established* within the region of normal blackening.

This equality of intensity may, however, vanish when the electrical conditions of the discharge are varied, either by changes in the current strength, the voltage, or the frequency of the spark, or by the presence in the electrode of other elements besides P and A . Variations of this kind in the ratios of the intensities occur, for instance, in a very pronounced measure when one of the lines of the pair under comparison appertains, *e.g.*, to the arc spectrum of A , and the other to the spark spectrum of P . It may likewise occur in cases where both lines are due to the same atomic state (that of neutral atoms or that of ions). It

is, however, a very difficult matter to maintain constancy in the conditions of the discharge by controlling the electric conditions, and in many cases it is quite impossible.

Hence the selected pairs of comparison lines should be of a kind which remain *wholly* unaffected by variations in the conditions of the discharge. Pairs of this kind, however, are scarce. It therefore became necessary to establish a reliable and easily manageable criterion for maintaining correct conditions in the electric discharge. In view of the fact that the conditions of the luminosity are governed by those of the discharge, while it is a primary requirement that the *conditions of luminosity* should be reproducible, it readily suggested itself to *employ the latter themselves as a means of defining the conditions of the discharge*. A readily recognizable criterion, for instance, is furnished by the ratio of the intensities of the arc-lines to those of the spark-lines of the primary substance, this ratio being dependent upon the nature of the excitation. If the latter be so arranged that a certain arc-line P_A of the primary substance may appear of an intensity which is always equal to that of an adjacent spark-line P_S , this signifies that in all these cases the conditions of the luminosity were alike. *The conditions of the discharge are thus recognized, without recourse to the measurement of the electrical quantities, by the emission of the spark itself*. This accordingly disposes of the question as to the practicability of reproducing the conditions of the discharge in that their reproduction is always practicable by this method in the appropriate relation.

There remains accordingly to be considered the dependence of the intensity ratio upon the optical arrangement, the nature of the spectrograph, and the sensitivity of the photographic plate. None of these factors affect the result if the spectrum-lines of A and P which are to be compared are spectroscopically adjacent to one another. Their small distance apart on the spectrogram incidentally facilitates their visual comparison and ensures generally a like blackening of the background.

We thus see established the practicability of an *absolute* system of chemical analysis capable of being carried out with any appropriate form of apparatus. *In the preparation of analytical tables*, of which we shall submit a few later on, the procedure is as follows. Sparks should be discharged between electrodes $P + a\% A$, $P + b\% A$. . . etc. under normal conditions of excitation (see Chapter III). In the resulting spectrograms all those (most nearly adjacent) pairs of lines of P and A having approximately like intensities should be sought and their wavelengths determined. With the aid of tables (*e.g.* those in Kayser's *Handbuch der Spektroskopie*) the lines corresponding to like atomic states (*i.e.* those appertaining to neutral atoms or ions respectively, or

of like series character) should be ascertained. All pairs should there-upon be rejected which consist of an arc-line and a spark-line. Next, new electrodes should be prepared having concentrations a_1, a_2, a_3 , or b_1, b_2, b_3 respectively, etc., where the a_i or b_i values differ from a and b respectively to such an extent that it becomes highly probable that further spectrograms will furnish a P - A pair of lines of exactly equal intensity. When electrodes of such a composition have been found the conditions of the discharge should be varied by varying the self-induction and the capacity in the spark circuit, if necessary also the voltage or amperage of the primary circuit of the induction-coil or transformer,¹ noting the range of the conditions of excitation within which the equality of intensity is maintained. Another spectrogram should then be obtained with an excitation midway between these ascertained admissible limits and a pair of lines of the *primary substance* selected which under this excitation exhibits *approximately* like intensity but shows marked variations under other excitations. In most cases this pair will consist of a spark-line and an arc-line of P . We call these two lines the *fixation pair*.

When applying this method for determining A in P the conditions of excitation should be so adjusted that this fixation pair of P may be of approximately equal intensity. This *one* condition requires to be satisfied (which can be easily done) in order that the analytical table of homologous pairs may be applied.

The pairs of lines $(P-A)_1, (P-A)_2 \dots$ which at concentrations $a, b \dots \% A$ were found to exhibit like intensities shall be called *homologous pairs*. Their equality of intensity is a single valued measure of the amount of A present in P . The utility of this pair for analysis increases

with its insusceptibility to variations in the conditions of discharge and with the degree of uniformity in the appearance of the lines as regards width and definition.² The concentration at which the pair of lines has like intensity we will call its *fixed point*. This fixed point be-



FIG. 21.

¹ All that is necessary is to avoid such intense increases in the energy as to cause the electrodes to become heated. This may be accomplished, even when the spark energy is very high, by reducing the frequency in the primary circuit, which is an easy matter when using an induction coil with rotating interrupter.

² In this connection attention may be drawn to a difficulty which occasionally arises in the identification of the lines of like intensity. When a line a of a homologous pair $a c$ happens to lie close to a very strong spectrum-line b , an optical illusion may easily vitiate the result. This may be obviated by placing a white or grey strip of paper between a and c (see fig. 21).

comes more definite and the analysis accordingly more exact as the concentrational sensitivity of the A -line in the homologous pair increases.

In fig. 22 P_1, P_2, P_3, P_4 represent spectrum-lines of the primary substance, while A is a line due to the admixture. The length of the

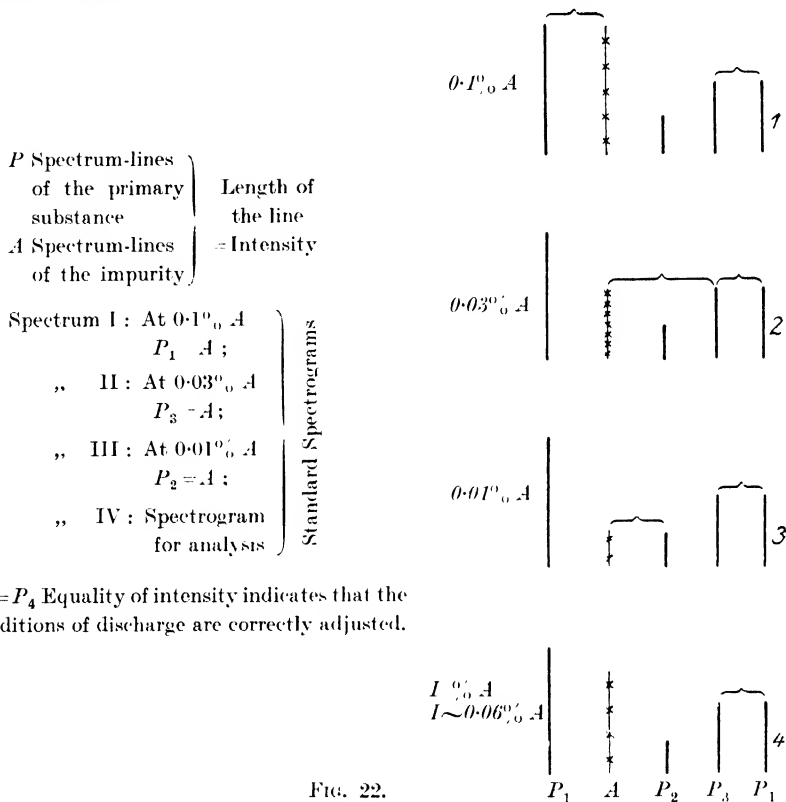


FIG. 22.

lines is made to furnish a measure of their intensity. The pairs of lines AP_1, AP_3, AP_2 respectively have their fixed points at $0.1, 0.03, 0.01\% A$ in P respectively. P_3 (the atom-line) and P_4 (the ion-line) form the fixation pair for the conditions of discharge. Spectrograms of the nature of Nos. 1-3 form the basis for the table of homologous pairs of lines. Let No. 4 represent a spectrogram taken for the analysis. Since in the latter A lies between P_1 and P_3 it follows that the concentration x is between 0.1 and 0.03 per cent.

In fig. 23, which reproduces a spectrogram of $\text{Sn} + 0.1\% \text{Pb}$, is shown the invariance of the homologous pairs of lines which obtains despite varying conditions of the discharge as well as the very pronounced variations in the intensity of the fixation pair R which are occasioned by the conditions of the discharge. It will be seen to what pronounced extent the fixation pair, hence also the conditions of the

discharge, may be varied without causing any perceptible alterations in the intensities in the homologous pair.

The fixation pair is entirely independent of the nature of the element A which is to be determined as a percentage component of P . It fixes the conditions of discharge for all homologous pairs of lines of all conceivable A -elements in the same primary substance.

This elimination of the influence of the discharge conditions automatically renders the equality of intensity of the homologous pair independent of other admixtures in the material of the electrodes. Nevertheless we have submitted this conclusion to verification by comprehensive experiments,¹ some of which we propose to describe.

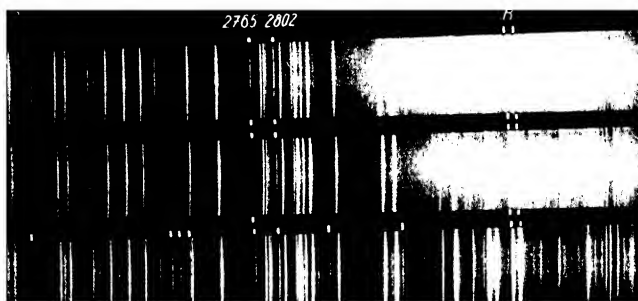


FIG. 23.—Reproduction of Conditions of Discharge.

The pair of lines marked by the letter R (Sn 3352, 3331) varies in a pronounced degree with the conditions of discharge. The marked lines (lead 2802, tin 2765) are independent of the discharge conditions. The middle spectrum (showing a fixation pair R of equal intensity) conforms to the proper conditions of discharge.

The fixed point of these lines is at 0.1% Pb. in Sn.

To begin with, an alloy of lead and tin in the atomic ratio 1 : 1 was prepared. Small quantities of this alloy were melted together with cadmium and bismuth, so that electrodes of the compositions $\text{Cd} + n\% \text{Pb} + n\% \text{Sn}$ and $\text{Bi} + n\% \text{Pb} + n\% \text{Sn}$ respectively were rendered available. The ratio of the intensities of the lead and tin lines was for both primary substances entirely the same. It also remained constant when the concentrations n were varied within wide limits, which, as a matter of fact, already follows from the equal concentrational sensitivity of an A -line in different primary substances (cf. Chapter II, e).

The like experiment was repeated with alloys of cadmium and bismuth which were melted in various concentrations together with

¹ It goes without saying that care must be exercised to ensure that the other admixtures may not by any chance exhibit spectrum-lines at a place which is occupied by a line of the homologous pair. In this connection see W. GERLACH and E. SCHWEITZER, *Bem. zu Hüttig, Zeits. f. analyt. Chemie* 77, 213 (1929).

lead and tin as primary substances. Again the ratio of the intensity of the cadmium and bismuth lines was maintained, independently of the primary substance, at all concentrations.

A simple experiment furnishes an even more convincing proof of the general validity of this experimental result. Spectrograms of tin + 1% lead were made and the homologous pairs of lines established therein. The lower electrodes were then replaced in succession by all kinds of *metal electrodes free from tin and lead*, viz. cadmium, bismuth, copper, silver, and gold, the spark being thus made to pass between an electrode of these elements and the upper tin + 1% lead electrode. *In the resulting spectrograms there were no discernible variations in the homologous pairs (Sn - Pb).* During the passing of the sparks very small quantities of the upper Sn + 1% Pb electrode are transferred to the lower pure metal electrode. If now we replace the upper (Sn - Pb) electrode likewise by a fresh electrode of the pure metal of the lower electrode the previously deposited small quantities of the Sn - Pb electrode are volatilized by the first sparks. Even now the spectrograms are found to exhibit exactly the original ratio Sn : Pb.

The fixed point of the homologous pairs of lines is thus entirely independent of the nature and the vapour pressure of the elements which are simultaneously rendered luminous in the discharge.

We were able to show the same to hold good for the atmosphere through which the spark passes. *It was entirely immaterial in the effect upon the intensity ratio of the homologous lines* whether the spark-gap was situated in air, oxygen, nitrogen, hydrogen or argon, whereas the absolute intensities and also the intensity ratios of *other, i.e. non-homologous*, lines exhibit marked variations.

The most rigid test which can be applied to establish the independence or otherwise of the homologous pairs of lines in relation to any influences which may be exercised by the luminous excitation is the examination of the alloys $P + a, b, c \dots \% A$ in solution. We have to this end dissolved various series of alloys in acids and, using a spark from the solution in such a way as not to introduce errors inherent in the spark-gap (cf. Chapter III, pp. 39 *et seq.*), we have been able to establish that the homologous pairs of lines maintain their invariable character unaffected by the concentration n in $P + n\% A$, by the nature of the acid, by the concentration of the solution, and finally by the addition of other salts (cf. figs. 24, 25, 26). Thus, in one of our experiments potassium chloride was added to a solution of zinc chloride and cadmium chloride (Zn : Cd = 1 : 1) until the solution contained 32% of KCl, yet there was no perceptible change in the intensity ratio of the zinc and cadmium lines.

The outcome of the experiments described above supplies a further

means ¹ of analyzing alloys of *which there are neither specimens of known composition nor of which homologous pairs are known.*

For instance, let it be required to analyse an alloy of copper and tin $\text{Cu} + x\% \text{ Sn}$, for which no homologous pairs are known. We proceed by dissolving a weighed quantity of this alloy in an acid, adding to the resulting solution a definitely known amount of a lead salt. The spark

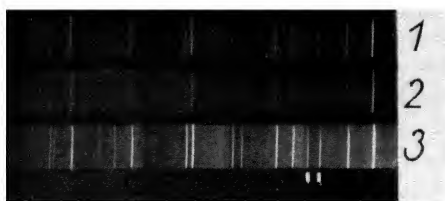


FIG. 24.—Spectrum of tin + 1% lead. Spectrum No. 1: Solid electrodes. Spectrum No. 3: Chloride solution. The spectrum shows complete equality in the marked homologous pair independently of the type of the electrodes.

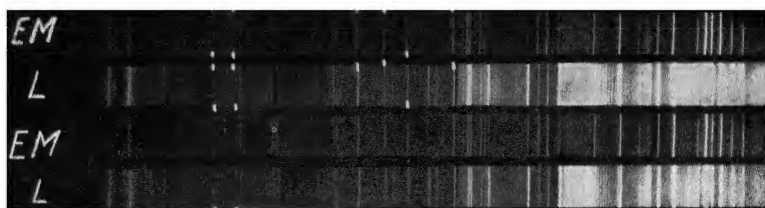


FIG. 25.—Solid electrodes (*EM*) and chloride solution (*L*). These show like intensity ratios of the lines of tin to those of lead.

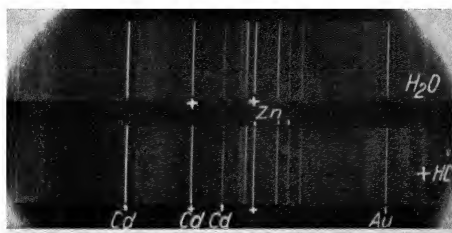


FIG. 26.—Zinc nitrate and cadmium nitrate (Zinc : Cadmium in ratio 1 : 1). Upper spectrum: Aqueous solution. Lower spectrum: With copious addition of hydrochloric acid.

from the solution will now show the spectrum-lines of copper, tin, and lead. Of the two latter elements we know, however, a large number of homologous pairs of lines. From these we are able to determine the ratio of $\text{Sn} : \text{Pb}$ in the solution and from the quantity of lead, known in

¹ W. GERLACH, *Metallwirtschaft*. December 1928, No. 49.

terms of grammes or atoms, we find the quantity of tin which was contained in the dissolved quantity of the alloy. Since the intensity relations of the homologous pairs Sn – Pb are entirely independent of the nature of the solution, a way can always be found of getting the three salts completely dissolved.

We append a few tables of homologous pairs of lines. The conditions of the discharge for these analyses are established by obtaining, before proceeding with the analysis, spectra of either the tin or the lead under various electrical conditions. The condition of the discharge which was laid down as normal was that which established equal intensities either of $\text{Sn}^+ 3352 = \text{Sn } 3331$ or of $\text{Pb}^+ = 2562 = \text{Pb } 2657$, the latter pair being the better of the two.

TABLE I

TABLE OF HOMOLOGOUS PAIRS OF LINES IN THE SPECTRA OF TIN CONTAINING LEAD AS AN IMPURITY

WAVE-LENGTHS OF LINES	INTENSITIES EQUAL AT ATOMIC PER-CENTAGE Pb	DISTANCE $\delta \lambda$ BETWEEN LINES	REMARKS
λ Pb = 2833 Å λ Sn = 2851	10 ⁻¹	18	Very short exposure should be given in order that the intensities may be weak enough to establish equality—moderately invariant. ¹
λ Pb = 2663 λ Sn = 2661	10 ⁻²	2	Not separated in spectrographs of small resolving power. Very invariant.
λ Pb = 2802 λ Sn = 2851	3	49	Very invariant.
λ Pb = 4058 λ Sn = 3801	2	257	Give short exposure—large $\delta \lambda$ value very invariant.
λ Pb = 2614 λ Sn = 2594	1.3 ³	20	Equality of intensity very well observable.
λ Pb = 2823 λ Sn = 2765	1.3 ⁴	58	
λ Pb = 2873 λ Sn = 2765	0.6 ⁵	108	Given ample exposure, equality of intensity may be readily recognized—very invariant.
λ Pb = 2802 λ Sn = 2765	0.1	37	
λ Pb = 4058 λ Sn = 3656	0.06	404	Self-induction should not be too small in the secondary circuit—fairly invariant.
λ Pb = 2614 λ Sn = 2637	0.02	23	Long exposure—the lines present rather dissimilar appearances—moderately invariant.

¹ According to G. SCHEIBE and A. NEUHÄUSSER this pair maintains equality of intensity in the presence of over 10% of Pb. Nevertheless, this pair is ill adapted for the spectrometric measurement at *high Pb-concentrations*. This is because the Pb-line 2833 is the strongest absorption line and has therefore a very small relative (or concentrational) sensitivity. Moreover, owing to the absorption in the lead vapour cloud its intensity is largely affected by its thickness and density, and hence by the intensity of the discharge and the thickness of the electrodes.

² According to SCHEIBE and NEUHÄUSSER likewise 10%.

³ According to SCHEIBE and NEUHÄUSSER: 2%. 2614 is a strong absorption line. We have worked with a very low vapour density in the spark and find our result confirmed thereby. Cf. also Note 1, p. 84, where SCHEIBE and NEUHÄUSSER likewise obtain a *higher* fixed point than ours (cf. Note 1, p. 84).

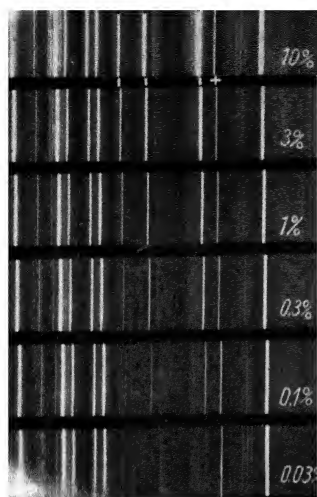
⁴ According to SCHEIBE and NEUHÄUSSER: 1.1%, *i.e.* in agreement with our value within probable limits of error.

⁵ According to SCHEIBE and NEUHÄUSSER likewise 0.6%.

TABLE II

TABLE FOR THE ANALYSIS OF Cd IN Sn (*see* fig. 27)

WAVE-LENGTHS OF LINES A	INTENSITIES EQUAL AT PERCENTAGE BY WEIGHT OF Cd	DISTANCE $\delta \lambda$ BETWEEN LINES	REMARKS
λ Cd = 3404 λ Sn = 3331	10	73	Give short exposure—fixed point sharply defined—extremely invariant.
λ Cd = 3404 λ Sn = 3656	2	202	Fixed point sharply defined—fairly invariant.
λ Cd = 3404 λ Sn = 3142	1.5	262	Fixed point very sharply defined—extremely invariant.
λ Cd = 3404 λ Sn = 3219	0.5	185	Give long exposure—Fixed point very sharply defined—extremely invariant.
λ Cd = 3466 3468 λ Sn = 3656	0.3	189	Fixed point somewhat indefinite—very invariant.
λ Cd = 3611 3615 λ Sn = 3656	0.2	44	Fixed point somewhat indefinite—very invariant.
λ Cd = 3466 3468 λ Sn = 3219	0.15	248	Give long exposure—Fixed point sharply defined—very invariant.
λ Cd = 3404 λ Sn = 3224	0.1	180	Give long exposure—Fixed point very sharply defined—extremely invariant.
λ Cd = 3466 3468 λ Sn = 3224	0.05	243	Give long exposure—Fixed point sharply defined—very invariant.
λ Cd = 2288 λ Sn = 2282	0.01	6	Give extremely long exposure—Fixed point somewhat indefinite—2288 Cd should be separated from 2287 Sn—very invariant.



Wavelengths from right to left :

$$\left. \begin{matrix} 3615 \\ 3613 \\ 3611 \end{matrix} \right\} (\alpha) \quad \left. \begin{matrix} 3468 \\ 3466 \end{matrix} \right\} (\beta) \quad 3404 (\gamma)$$

Cd γ at 3%, Cd is still a little stronger than Sn 3656 (fixed point of these two lines at 2%, Cd); Cd β at 0.3%, Cd is of equal intensity to Sn 3656; the fixed point of Cd γ and Sn 3656 lies between 0.3% and 0.1% Cd.

FIG. 27.

Standard Scale, Tin + α %, Cadmium.

The tin-line (+) (3656 Å) is compared with the three lines of the cadmium triplet ().

TABLE III
TABLE FOR THE ANALYSIS OF Bi IN Sn

WAVE- LENGTHS OF LINES A	INTENSITIES EQUAL AT PER- CENTAGE BY WEIGHT OF Bi	DISTANCE $\delta \lambda$ BETWEEN LINES	REMARKS
λ Bi = 3068 λ Sn = 3009	10	59	Give very short exposure—very invariant.
λ Bi = 2697 λ Sn = 2765	7	68	Give liberally long exposure—Fixed point very sharply defined—extremely invariant.
λ Bi = 2938 λ Sn = 3142	3	204	Fixed point very sharply defined—very invariant.
λ Bi = 2628 λ Sn = 2637	0.7	9	Give intense exposure—Fixed point not well defined owing to dissimilar appearance of lines—fairly invariant.
λ Bi = 2938 λ Sn = 2765	0.7	173	Fixed point very sharply defined—extremely invariant.
λ Bi = 3068 λ Sn = 3142	0.2	74	Fixed point very sharply defined—very invariant.
λ Bi = 3068 λ Sn = 3219	0.04	151	Give intense exposure—moderately invariant.
λ Bi = 3068 λ Sn = 3224	0.007	156	Give very intense exposure—fairly invariant.

TABLE IV

TABLE FOR THE ANALYSIS OF TIN IN LEAD

WAVE-LENGTHS OF LINES A	INTENSITIES EQUAL AT ATOMIC PER-CENTAGE OF Sn	DISTANCE $\delta \lambda$ BETWEEN LINES	REMARKS
λ Sn = 2572 λ Pb = 2629	10	57	Exposure not too short - extremely invariant.
λ Sn = 2422 λ Pb = 2412	5	10	Extremely invariant.
λ Sn = 2572 λ Pb = 2657	0.6	85	Give intense exposure—very invariant.
λ Sn = 2422 λ Pb = 2389	0.6	33	Give intense exposure very invariant.
λ Sn = 2707 λ Pb = 2629	0.4	78	Extremely invariant.
λ Sn = 2355 λ Pb = 2389	0.2	34	Give intense exposure—fairly invariant.
λ Sn = 2707 λ Pb = 2657	0.04	50	Give intense exposure very invariant.

TABLE V

TABLE FOR THE ANALYSIS OF Bi IN Pb

WAVE-LENGTHS OF LINES A	INTENSITIES EQUAL AT PER-CENTAGE BY WEIGHT OF Bi	DISTANCE $\delta \lambda$ BETWEEN LINES	REMARKS
λ Bi = 2731 λ Pb = 2657	5	74	Fixed point sharply defined—Give intense exposure—fairly invariant.
λ Bi = 2781 λ Pb = 2657	1.5	124	Fixed point somewhat ill defined—Give intense exposure—fairly invariant.
λ Bi = 3025 λ Pb = 3221	1.5	196	Fixed point sharply defined—very invariant.
λ Bi = 3068 λ Pb = 3221	0.07	153	Fixed point sharply defined—very invariant.

TABLE VI

HOMOLOGOUS LINES IN IRON + SILICON ¹

WAVE-LENGTHS OF THE PAIR OF LINES A	INTENSITIES ALIKE AT PERCENTAGE BY WEIGHT OF Si	HOMOLOGY OF LINES	REMARKS
λ Si = 2528.5	3.74	Si = 2528.5 Si I	
λ Fe = 2521.7		Fe = 2522.9 Fe I	
λ Si = 2881.7	1.2	Si = 2881.7 Si I	Variable, subject to conditions of discharge.
λ Fe = 2880.7		Fe = 2880.7 Fe II	
λ Si = 2881.7	0.80—0.88	Si = 2881.7 Si I	Very invariant.
λ Fe = 2926.6		Fe = 2926.6 Fe I (?)	
λ Si = 2524.1	0.5	Si = 2524.1 Si I	Large dispersion required.
λ Fe = 2523.6		Fe = 2523.6 Fe I	

I indicates neutral atom.

II indicates simple positive ion.

(?) denotes that the homology is doubtful.

The pairs 1, 3, 4 will be invariant with respect to the conditions of the discharge within wide limits.

¹ According to SCHEIBE and NEUHÄUSSER, *Z. f. angew. Chemie* 41 (1928), 1218.

TABLE VII

HOMOLOGOUS PAIRS OF LINES IN IRON + MANGANESE ¹

WAVELENGTHS OF THE PAIR OF LINES A	INTENSITIES EQUAL AT PERCENTAGE BY WEIGHT OF Mn	HOMOLOGY OF LINES
λ Mn = 2933.0	1.4	Mn = 2933.0 Mn II
λ Fe = 2923.8		Fe = 2923.8 Fe I
λ Mn = 2939.3	0.95	Mn = 2939.3 Mn II
λ Fe = 2923.8		Fe = 2923.9 Fe I
λ Mn = 2949.4	0.9	Mn = 2949.4 Mn II
λ Fe = 2944.4		Fe = 2944.4 Fe II

I indicates neutral atom.

II indicates simple positive ion.

Only the last homologous pair will be largely independent of the conditions of the discharge.

HOMOLOGOUS LINES IN GOLD + LEAD ²

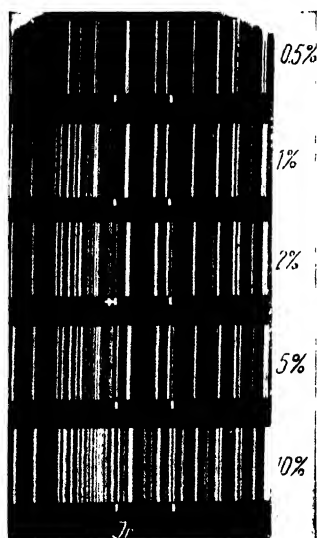
Au 2544 } of equal intensity at 0.8° Pb.
Pb 2614 }

¹ According to SCHEIBE and NEUHÄUSSER, *Z. f. angew. Chemie*, 41 (1928), 1218.

² According to W. GERLACH and E. SCHWEITZER, *Z. f. anorg. u. allg. Chem.* 173 (1928), 104.

TABLE VIII
IRIDIUM IN PLATINUM (*see* fig. 28)

SPECTRUM LINES WITH WAVELENGTHS		INTEN- SITIES EQUAL AT 1% PERCENT- AGES OF	IRIDIUM CONSTANT DETERMINED THUS :
Ir A	Pt A		
3220.8	3301.85	32	Photometrically extrapolated. Caution needed owing to presence of Na 3302.94.
3220.8	3204.1	26.8	Interpolated between 26 and 30%.
2936.7	2919.3	20	Standard alloy.
2836.4	2834.7	19	Large dispersion required.
2840.2	2834.7	19	
2694.2	2698.4	15	Brief exposure. Standard alloy.
2934.6	2919.3	13.3	Photometrically interpolated between 12 and 14%.
2899.2	2834.7	12.8	Interpolated between 12 and 14%. Large dispersion required.
3133.6	3156.6	ab. 10.4	Not invariant. Photometric readings range from 9.5 to 11%.
3220.8	3200.7	ab. 9.3	Photometrically interpolated. 3156.6/3200.8, disturbed by strong adjoining Pt lines.
2934.6	2921.4	6.8	Interpolated between 5 and 7%.
2936.7	2921.4	4.9	Interpolated between 3.5 and 5%.
2924.8	2919.3	4.7	Interpolated between 3.5 and 5%.
3220.8	3230.3	2	Standard alloy.
3220.8	3233.4	1.64	Interpolated between 1.5 and 2%.
2924.8	2921.4	1.56	
3220.8	3212.5	0.3	Extrapolated from 0.5.



The spectrum apparatus should have a sufficiently large dispersion. Above 3% Iridium a low luminous excitation should be applied. The concentration numbers signify grammes of Iridium per 100 grm. of alloy.

FIG. 28.—Platinum + Iridium.
Standard Scale. Homologous pair at 2%
Iridium (Pt 3250.4, Ir 3220.8).

TABLE IX
RHODIUM IN PLATINUM

SPECTRUM LINES WITH WAVELENGTHS		INTEN- SITIES EQUAL AT $\frac{0\%}{\%}$	RHODIUM CONTENT DETERMINED THUS :
Rh	Pt		
3958.8	3923.0	7.5	Extrapolated from 5%.
2510.7	2513.9	5	Chemical analysis.
3942.7	3948.4	5	Chemical analysis.
2520.5	2513.9	4	Interpolated between 3 and 5%.
3856.5	3923.0	4	Do. do.
2475.6	2488.7	3	Chemical analysis.
2510.7	2488.7	2.5	Chemical Analysis.
2520.5	2488.7	1.5 ¹	Interpolated between 1 and 2%.
3958.8	3948.4	1.4	Do. do.
3658.0	3638.8	1.2	{ Interpolated between 1 and 2%, photo- metrically measured.
2475.6	2482.1	1.1	
3597.2	3638.8	1	{ Interpolated between 1 and 2%, photo- metrically measured ; chemical analysis.
3596.2			
2510.7	2482.1	0.8	Interpolated between 0.5 and 1%.
3658.0	3706.7	0.6	Do. do.
2520.5	2482.1	~ 0.5	Chemical analysis.

¹ Caution should be exercised where the specimen contains a large proportion of palladium (Pd-line 2488.9).

We will now append a few diagrams of spectra from which the position of the spectrum-lines for the analysis of platinum may be readily recognized.²

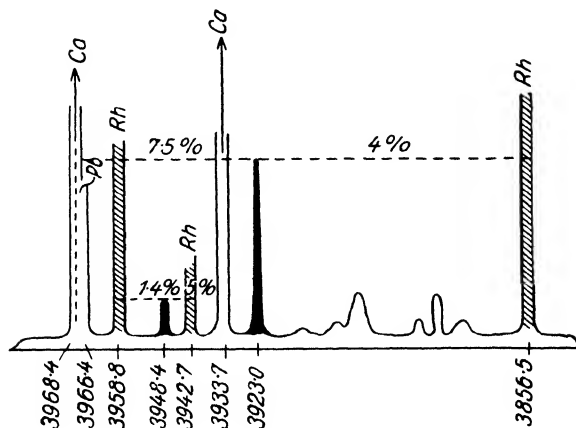


FIG. 29.

² For further particulars see W. GERLACH and E. SCHWEITZER, "Spektralanalytische Schnellmethode zur quantitativen Bestimmung von Iridium, Rhodium, Palladium in Platin. VIII. Mitteilung," *Z. f. anorg. u. allg. Chemie.* 181. (1929), 103.

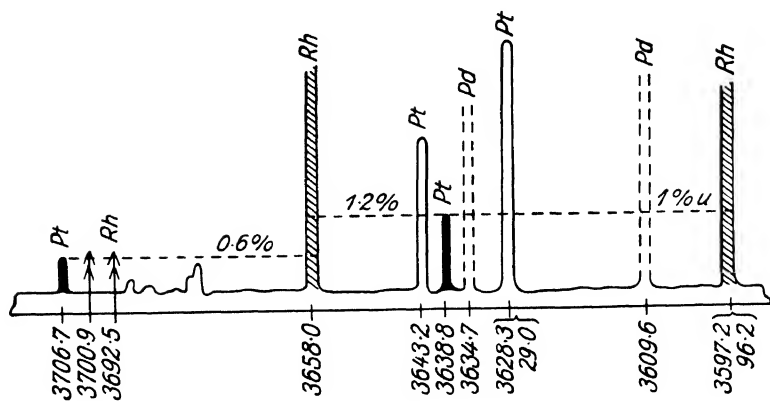


FIG. 30.

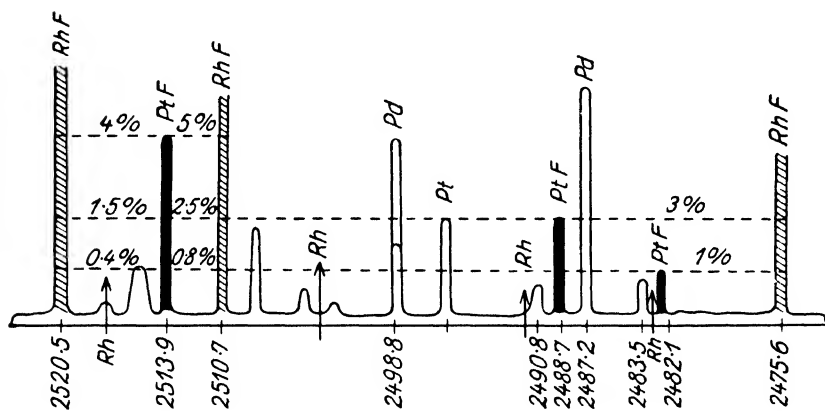


FIG. 31.

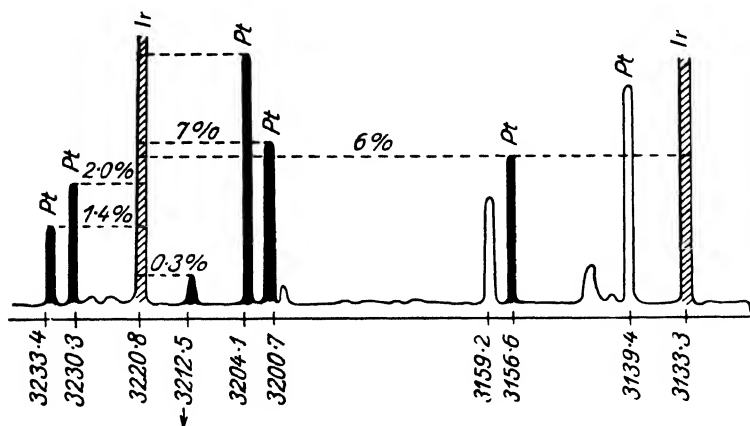


FIG. 32.

(d) THE METHOD OF HOMOLOGOUS PAIRS AS APPLIED TO THE ANALYSIS OF SOLUTIONS

In the preceding section it was shown that homologous pairs which in a solid alloy $P + n\% A$ have their fixed point at $n = a$ maintain this point of fixation when the alloy is dissolved in an acid. It has thus

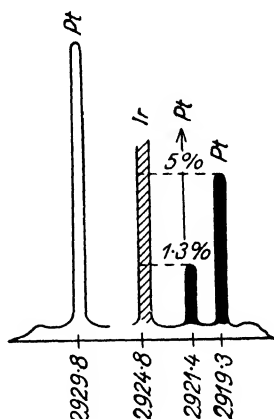


FIG. 33.

been demonstrated that the absolute method there described is equally applicable to sparks from liquids for the analysis of the dissolved substance. This accordingly establishes also a method of quantitative analysis of salts.

This constancy of the fixed point under widely varying conditions of excitation is decidedly striking. It would be reasonable to expect that even with very invariant pairs there might be nevertheless a displacement of the intensity relations. As a matter of fact there are cases where there are noticeable, though small, divergencies. We will therefore not omit to describe the experiments which we have made in this connection.

By way of a spark-gap for solutions we employed the arrangement represented in fig. 12. An alloy of Sn + 1% Pb was dissolved in pure hydrochloric acid and the solution concentrated nearly to the point of saturation. The resistance in series with the spark-gap was so adjusted (by the addition of small drops of acid) that the spark passed to the surface of the meniscus and just gave rise to incipient spraying. The spark remained fairly weak in luminosity, nevertheless the water bands did not appear with the same intensity as was the case when a very large resistance was used. An out-of-focus image of the spark was formed upon the slit of the spectrograph.

In the spectrogram the lines Pb 2614 and Sn 2594 had fairly exactly equal intensities, whereas by the use of solid electrodes we had found

the fixed point of this homologous pair to be at 1.3%. Here, then, we established a pronounced difference as compared with the spark from the liquid. When, however, we proceeded to take the spark spectrogram between solid electrodes under the same conditions as those obtaining in the liquid spark-gap, *i.e.* with the same resistance in series with it and a correspondingly small intensity of excitation (luminous intensity, perhaps, 1000 times less) it was found that the intensities of the lines named were alike at about 1%.

This displacement of the fixed point is due to the self-absorption of the line 2614 of lead. The intensity of this line is for this very reason not entirely independent of the conditions of the discharge since great vapour density causes it to be too strongly absorbed.¹ We have deliberately selected this case because it shows that in analyses of this kind it is necessary always to take into careful consideration all physical facts; on the other hand, it also demonstrates that the possible errors are nevertheless very small in that the two fixed points (1.3% with solids and a *little* above 1% with solutions) diverge by a little more than the limit of error of 10%. When the lead concentration is small this difference naturally becomes still smaller, since the amount of absorption diminishes.

If the second arrangement with the large liquid electrode indicated in fig. 13 be employed and operated with the full energy of the transformer (which may be done since in this spark-gap the spraying remains within moderate limits even with intense spark discharges, and the spark does not leap to the metal cup containing the liquid), it is found that the fixed points of the solid alloys and their solutions approach one another still more closely.

These experiments lead to a new method for the analysis of solutions. Thus it may be required to ascertain the proportion of a metal in a solution or in any soluble substance, assuming that this one metal only is present. This can be accomplished by the addition of a known amount of another metal. This is best shown by an example.

We prepared solutions of salts of tin and lead respectively which contained an equal number of atoms of tin and lead. The solutions (in every case Sn : Pb = 1 : 1) had different concentrations (10 to 0.01%). Next, we melted down an alloy of equal parts of tin and lead together with cadmium in such proportions that the finished electrode contained 10% (Sn + Pb) and 90% Cd. We then compared the spectra of the

¹ Cf. Table I, p. 75. SCHEIBE even finds 2% to be the fixed point. Obviously he operated with a still greater vapour density in the spark (possibly with an excessively hot electrode). We have repeatedly verified the fixed point of this homologous pair of lines Pb 2614 and Sn 2594, and have found it to be at 1.3%. However, when using an alternating current transformer with greater energy we likewise found the fixed point to conform to a somewhat higher Pb-concentration.

solutions and those of the alloy and found that in both the intensity conditions of the homologous lines Sn : Pb were identical and entirely independent of the absolute concentration of the solution and any added substances in the nature of acids, alkalis, or salts. This absence of any influence on the part of these additions is frequently of practical importance, for, where the dissolved amounts of salt are very small the resistance in the spark-gap will be very great and the line-spectrum becomes faint. The band-spectrum, if anything, however, increases in intensity. Solutions of this kind should preferably be rendered better conductive by the addition of a little acid (HCl).

Equality was found for certain pairs (Sn, Pb), *i.e.* homologous lines were found having their fixed point at 100%. Where now a solution containing Pb is to be analysed with respect to the latter, known quantities of Sn should be added to this solution until these particular pairs of lines become of equal intensity. The amount of tin which it was necessary to add to a given quantity of the solution under test will then be equal to the amount of lead contained therein.

Hüttig and Thurnwald¹ have also used this procedure, though in a manner which is open to objection in that they compared lines which were not invariant.² Nevertheless part of these investigations completely confirm our results.

Thus it was established experimentally that solutions containing zinc and silver furnish two definite lines of equal intensity (Zn 3345, Ag 3383) when the concentration *by weight* in grammes Zn : Ag was 20 : 1. We append in this connection an extract from a table, which shows that *this ratio is independent of the absolute concentration* in that equality of intensity obtained at the following concentrations :

per 100 c.c. of solution.

Grammes Zn	0.5	0.4	0.3	0.15	0.1	0.05	0.04	0.01	0.0075	0.005
Grammes Ag	0.025	0.02	0.015	0.0075	0.005	0.0025	0.002	0.0005	0.000375	0.00025

The accuracy was estimated to be 20-25% of the absolute amounts.

(e) THE METHODS OF SUBSTITUTION

The practicability and, given this, the applicability of absolute analysis by the method of homologous pairs is subject to two conditions, both of which are inherent in the nature of the special analytical

¹ G. HÜTTIG and H. THURNWALD, *Z. f. anal. Chem.* 76, 260, 355 (1929). Cf. also F. GROMANN, *Z. f. anorg. u. allg. Chem.* 180 (1929), 257.

² W. GERLACH and E. SCHWEITZER, *Z. f. anal. Chem.* 77, 213 (1929).

problem involved : The A -lines should have P -lines as neighbours in the spectrum, both being appropriate in character and intensity, and there should be a sufficient number of A -lines of a kind which do not coincide with very faint P -lines or lines of other impurities which may be present. These conditions are particularly well fulfilled in the analysis of platinum with respect to the presence of other heavy metals, as may be judged from the great number of homologous pairs of lines within a narrow range of concentration (see Tables VIII and IX). It is poorly satisfied through lack of suitable P -lines in such cases as the determination of bismuth in lead (Table V) and through lack of A -lines in such analyses as that of lead in gold.

In what follows we shall describe two procedures whereby even in the latter cases an absolute method of analysis by reference to homologous pairs of lines becomes practicable. The essence of the procedure consists in *artificially increasing the number of the P -lines or that of the A -lines* and thereby creating suitable "substituted" P -lines and A -lines respectively as a means of obtaining homologous pairs of lines.

Let a primary substance P be such that it presents no spectrum lines suitable for the analysis of A (fig. 34). This being the case, a spectrogram of a specimen of $P + a\%$ A should have photographed above it a spectrogram of another element S , which we call the "substituted spectrum." The intensities of the S -lines and those of the A -lines should then be compared. If now the intensities of the S -lines be coupled in a definite manner with the spectrum of P , it is obvious that all S -lines, when compared with the A -lines, will behave exactly as if they were P -lines. S takes the place of P . By a suitable choice of the substance S it will in every case be practicable to ensure that a sufficient number of S -lines of appropriate intensity for the creation of homologous pairs (S, A) may be present.

The coupling of S with P is effected in a similar manner to that of the procedure of fixing the conditions of the discharge, as explained above, or in that of establishing the homologous pairs, viz. by the equality of intensity of two specific lines of S and P which have the quality of remaining unaffected by variations in the conditions of discharge. To this end all that is necessary is to take a series of spectra of the test substance $P + a\%$ A , giving the same exposure in each case, and to photograph above each of these spectrograms, a spectrum of the substituted substance, appropriately varying the time of exposure from one spectrogram to the next. Next, pairs of spectra should be selected in which the coupling lines S - P are of equal intensity, and from the homologous pairs S, A the pair should be sought which has its fixed point at $a\%$.

It is not necessary to photograph the S spectrum *above* the spectrum

of the specimen. It may also be placed between two successive spectra of $P + a\%$ A , or by an upward or downward displacement of the plate it may be projected upon either half of the spectrum of the specimen. Lastly, the plate may be displaced by a very small amount in the direction of the dispersion, if thereby the mutual positions of the P , S and A -lines can be rendered more favourable. Thus, in the example given in Table X the tin-line 3219 does not appear separated from the lead-line 3221 where the dispersion of the apparatus happens to be small. The two may, however, be separated at once by displacing the plate by a few widths of the lines.

In the diagram of fig. 34 these appearances are shown graphically. Three spectra are there drawn one above the other, in which the lengths of the lines indicate the relative intensities. The lines marked P appertain to the primary substance, those marked A to the admixture which is to be determined quantitatively, and those marked S to the auxiliary metal. From the upper spectrum of $P + a\%$ A it will be seen that for the admixture lines 4 and 6

there are no lines of the primary substance adapted for comparison, neither in position nor intensity. In the middle portion of the figure the substituted spectrum of a suitable substance S is shown projected at random upon the original spectrum.

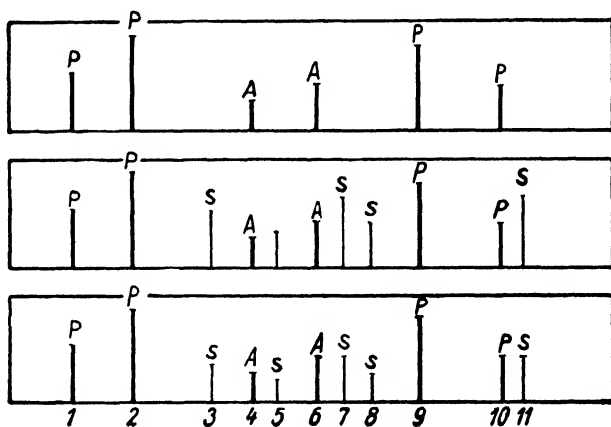


FIG. 34

In the neighbourhood of the admixture lines 4 and 6 there are now to be seen a number of possible comparison lines of S (e.g. 3, 5, 7, 8). For the mutual fixation of these spectra the time of exposure should now be so chosen that the homologous lines 10 (P) and 11 (S) become of equal intensity. This stage is indicated in the lower spectrum. It is always practicable to so arrange matters that the admixture lines 4 and 6 may be homologous, at least within narrow limits, with respect to neighbouring S -lines. Since we are able to optically reproduce the conditions of discharge, the components of the comparison and fixation pairs need only possess more or less invariant intensity conditions.

The method of substitution is completely independent of the optical arrangement, the manner in which the image is formed, the properties

of the lenses, prisms and plates, in the same way as the simple absolute method, provided the two spectrograms of the specimen and the substituted substance are taken under constant experimental conditions.

We now append a Table X for the quantitative analysis of bismuth in lead, where the ordinary absolute method has failed owing to the lack of homologous comparison pairs. The spectrum of tin serves as the substituted spectrum *S*. At the outset the conditions of discharge are so adjusted with the aid of spectrograms of tin that

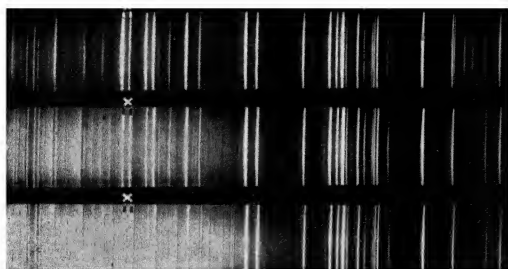


FIG. 35.

The lines of tin marked with a \times undergo pronounced variations under varying conditions of discharge. The middle spectrogram (equality of the fixation pair) conforms to the normal condition of discharge.

Sn 3352 and Sn 3331 present equal intensities (fig. 35). Under the conditions of discharge thus established, the spectrum of the substance which is to be analysed and the substituted spectrum should then be photographed one above the other in the manner shown below (fig. 36).



FIG. 36.—Method of the substituted auxiliary spectrum.

Bismuth in lead, tin furnishing the comparison spectrum. The comparison pairs and the coupling pair are invariant. Spectrogram No. 4 represents correct coupling. The various spectrograms differ by the respective times of exposure.

TABLE X

TABLE FOR THE DETERMINATION OF Bi IN Pb

I. Reproduction of the conditions of discharge.

$$\left. \begin{array}{l} \lambda \text{ Sn} = 3352 \text{ \AA} \\ \lambda \text{ Sn} = 3331 \text{ \AA} \end{array} \right\} \text{ must be of equal intensity ;}$$
the capacity in the discharge circuit being $C = 6000 \text{ cm.}$

II. Fixation of the auxiliary spectrum (Sn) ("Coupled pair.")

$$\left. \begin{array}{l} \lambda \text{ Sn} = 2422 \text{ \AA} \\ \lambda \text{ Pb} = 2412 \text{ \AA} \end{array} \right\} \text{ must be of equal intensity.}$$

This will occur when the ratio of the times of exposure is approximately :

$$E_{\text{Pb}+\alpha\gamma, \text{Bi}} : E_{\text{Sn}} = 12 : 1.$$

COMPARISON PAIRS

WAVE-LENGTHS OF LINES A	INTENSITIES EQUAL AT PERCENTAGE OF Bi	DISTANCE $\delta \lambda$ BETWEEN LINES	REMARKS
$\lambda \text{ Bi} = 2938$ or 2898 $\lambda \text{ Sn} = 2863$	10	75 35	Fixed point very sharply defined—very invariant.
$\lambda \text{ Bi} = 2938$ or 2898 $\lambda \text{ Sn} = 3009$	6	71 111	Fixed point sharply defined—very invariant.
$\lambda \text{ Bi} = 2731$ $\lambda \text{ Sn} = 2765$	3	34	Fixed point very sharply defined—Give ample exposure—moderately invariant.
$\lambda \text{ Bi} = 3068$ $\lambda \text{ Sn} = 3175$	3	107 107	Fixed point very sharply defined—Give very short exposure—very invariant.
$\lambda \text{ Bi} = 2938$ or 2898 $\lambda \text{ Sn} = 2851$	1.5	87 47	Fixed point very sharply defined—very invariant.
$\lambda \text{ Bi} = 3068$ $\lambda \text{ Sn} = 3009$	1	59	Fixed point sharply defined—very invariant.
$\lambda \text{ Bi} = 3025$ $\lambda \text{ Sn} = 3142$	0.6	117	Fixed point sharply defined—large self-induction—fairly invariant.
$\lambda \text{ Bi} = 2938$ $\lambda \text{ Sn} = 3142$	0.5	204	Fixed point very sharply defined—fairly invariant.
$\lambda \text{ Bi} = 2938$ $\lambda \text{ Sn} = 2765$	0.1	173	Fixed point very sharply defined—Give intense exposure—very invariant.
$\lambda \text{ Bi} = 3068$ $\lambda \text{ Sn} = 3142$	0.015	74	Fixed point very sharply defined—very invariant.
$\lambda \text{ Bi} = 3068$ $\lambda \text{ Sn} = 3219$	0.004	151	Give intense exposure—moderately invariant.

As another case for the application of the method of the substituted auxiliary spectrum we may instance the analysis of *gold* with respect to

small admixtures of *lead*. In this case the procedure consists in artificially increasing the number of the lead-lines present, that is of *A*, the application of the simple method having failed owing to the absence of a sufficiently large number of lead-lines. To this end the spectrum of $\text{Au} + n\% \text{ Pb}$ should be coupled with the spectrum of tin by the establishment of a pair Sn-Pb of equal intensity and comparing the lines of tin with those of the gold.

For the coupling with tin, the two lines of lead 2614 and 3684 may be employed, the latter giving the sharpest coupling. The conditions of the discharge should be fixed by the Pb-lines 2562 and 2657 by photographing in the first instance lead sparks under various conditions of the discharge and subsequently applying those conditions which established equal intensities of the lines of fixation named. Since now the coupling line 3684 is situated within a range the background of which is liable to be blurred by faint bands it is advisable so to arrange the choice of the discharge that the background may become as faint as possible. For this reason the capacity of the secondary circuit should always be 9000 cm. and the self-induction thereupon varied until the fixation pair attains equality of intensity. This procedure is particularly advantageous where the concentrations of lead are very small.

When carrying out the analysis the procedure is precisely the same as that described above; that is to say, above or between a series of spectrograms of the substance $\text{Au} + x\% \text{ Pb}$ which is to be analysed, spectra of tin should be photographed at different times of exposure (*e.g.* varied in the ratio of 1 : 2 : 4 : 8 : 16). The spectrum should then be sought in which the pairs of coupled lines Pb 3684, Sn 3656 and Pb 3614, Sn 2455 are of equal intensity, and in the subjoined table those pairs (Sn, Au) should be sought which have equal intensities. Table X then furnishes the required content of lead (*cf.* fig. 37).

Attention may here be drawn to a little artifice. In view of the fact that the gold spark has a small vapour pressure, whilst the tin spark has a high vapour pressure, it would in the ordinary course be necessary, for instance when coupling a specimen $\text{Au} + 0.01\% \text{ Pb}$ with tin, to give with the latter an exposure which is 200 times shorter. This is objectionable on practical grounds. To avoid this the tin should be diluted with cadmium, which yields a spectrum poor in lines, until the times of exposure required to establish the coupling become approximately equalized. The relative times of exposure may be somewhat as follows :

FOR COUPLING WITH :	TIME OF EXPOSURE FOR THE SPECIMEN OF GOLD	TIME OF EXPOSURE FOR 9 Cd + 1 Sn
1% Pb	1	4
0.2% Pb	1	1
0.04% Pb	4	1

For analyses of the order of magnitude of 0.01% Pb the substituted substance should be 19 Cd + 1 Sn. It may be accepted as superfluous to prove that the procedure is entirely independent of the concentration of tin in the auxiliary electrode.

A further difficulty may be overcome by the introduction of a substituted spectrum. In many analysis tables it would be practicable to give fixed points for far smaller additions, if there were not then a deficiency of very weak comparison lines known with certainty to appertain to the primary substance. Now, such desired comparison lines may be obtained by the introduction of a substituted spectrum. In the place of any other substituted spectrum we shall now employ that of the given specimen itself. This we show by the following data :

The last three homologous comparison pairs in the spectra of Sn + $a\%$ Pb according to Table I are :

Pb 2802 Å	}	of equal intensity at atomic- % 0.1
Sn 2765 Å		
Pb 4058 Å	}	of equal intensity at atomic- % 0.06
Sn 3656 Å		
Pb 2614 Å	}	of equal intensity at atomic- % 0.02
Sn 2537 Å		

The last pair in particular furnishes a rather indefinite fixed point. It would therefore be desirable to be able to replace the latter pair by another having a more sharply defined fixed point and, if possible, a fixed point in a lower position. To this end a spectrum I of the standard substance Sn + 0.01 Pb should be projected on the plate, giving a longer exposure T_1 . The plate should then be shifted by a few line-widths in the direction of dispersion (towards smaller or greater wavelengths), without, however, altering the arrangement in any way, and spectrum II taken of the same substance but at a shorter exposure T_2 . The spectra I and II should now be mutually fixed in such a way that equality of intensity may be established between the

Tin-Line	2455 Å in spectrum I
and Tin-Lines	} 2484 Å
	or } 2496 Å in spectrum II

This occurs approximately when the ratio of the times of exposure is $T_1 : T_2 = 10 : 1$. If now the Pb-line 2802 in spectrum I be compared with the Sn-line 2765 in spectrum II, it is found that

Pb 2802 Å in I	}	are of equal intensity at the atomic percentage 0.01
and Sn 2765 Å in II		

Also for the last pair but one we find

Pb 4058 Å in I	}	to be of equal intensity at the atomic percentage 0.006.
Sn 3656 Å in II		

These new fixed points provide a means of quantitatively determining very small traces of lead in tin and thereby serve to complete the original analysis tables. It will be seen that the potentialities of this method may be considerably extended in cases where certain purposes justify the trouble.

We confine ourselves to the particulars which we have given respecting these three aspects of the method of substitution. It may suffice to emphasize that these methods can be applied with exceptional ease and precision, and that their interpretation succeeds after comparatively short practice.

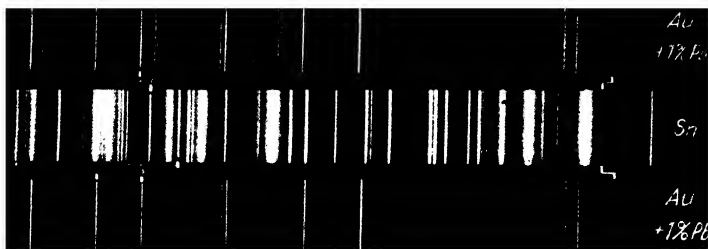


FIG. 37.—Method of the substituted spectrum for the analysis of lead in gold.

The substituted spectrum of tin is correctly coupled with lead. The marked lines on the left furnish the comparison lines of equal intensities of tin and gold (joined by dots). The fixed point lies a little below 1% Pb (see Table XI, pairs 2 and 3). On the right the coupling pair Sn 3656, Pb 3684 will be seen marked.

In many cases a proposed analysis bears within itself the character of a substitutional analysis. This happens when two admixtures A_1 and A_2 are contained in a primary substance in different proportions, in which case there are available for the analysis the homologous pairs of $P + m\% A_1$, $P + n\% A_2$, and $A_1 + p\% A_2$ (or $A_2 + p\% A_1$). We will describe this case by an example. In the instance in question two specimens of *lead* were to be examined with respect to tin and bismuth. The latter was present in a very small proportion. At the outset the Sn content was determined with the aid of Table IV. Let it be denoted by $a\%$. Next, with the aid of Table V it was ascertained that the proportion of Bi present was under 0.07%, being little less in the first specimen, much less in the second. Finally, by Table III the intensities of the Bi-lines were compared with those of the Sn-lines. This is permissible since, as we have repeatedly seen, it has been shown that the incorporation of an alloy $P + n\% A$ in any other metal does not perceptibly affect the fixed points of the homologous lines.

Supposing the comparison of tin and bismuth showing w to be the percentage of Bi with respect to *tin*, it follows that the concentration of bismuth in *lead* is $w \times a\%$.

TABLE XI (*see* fig. 37)

ANALYSIS TABLE

I. The conditions of discharge are approximately reproduced when, with a capacity $C = 9000$ cm. in the secondary circuit, the self-induction is so varied that in the spectrum of lead the lines

Pb⁺ 2562 }
Pb 2657 } become of equal intensity.¹

II. The coupling of the substituted spectrum ² Sn with the spectrum of the specimen is correct when the lines

Pb 3684 }
Sn 3656 }
Pb 2614 } are of equal intensity in pairs.
Sn 2455 }

COMPARISON PAIRS

No.	WAVELENGTHS OF THE COMPARISON LINES IN A UNITS		INTENSITIES EQUAL AT PERCENT- AGE BY WEIGHT OF Pb	REMARKS RESPECTING THE FIXED POINT
	SN	AU		
1	2408	2388	1.2	Fairly invariant, sharply defined.
2	2594	2642	0.9	Very invariant, sharply defined.
3	2524	2590	0.9	Slightly variable, sharply defined.
4	2851	2748	0.8	Fairly inv., fairly sharply defined, strong comparison lines.
5	2524	2544	0.65	Fairly inv., sharply defined, faint comparison lines.
6	2408	2376	0.45	Fairly inv., sharply defined.
7	2707	2748	0.2	Very inv., fairly sharply def., strong comparison lines.
8	2661	2701	0.2	Very inv., moderately sharply defined.
9	3009	3029	0.14	Extremely inv., sharply defined.
10	2594	2590	0.12	Slightly variable, fairly sharply def.
11	2707	2642	0.08	Very inv., fairly sharp.
12	2496	2511	0.056	Fairly inv., very sharply def.
13	2496	2544	0.046	Fairly inv., very sharply def.
14	2484	2511	0.046	Fairly inv., very sharply def.
15	2707	2701	0.04	Very inv., fairly sharply def.
16	2484	2544	0.035	Fairly inv., very sharply def.
17	2547	2511	0.035	Fairly inv., very sharply def.
18	2547	2544	0.028	Fairly inv., very sharply def.
19	2863	2884	0.01	Extremely inv., very sharply def.
20	2707	2590	0.008	Slightly variable, fairly sharply def.
21	2840	2884	0.006	Extremely inv., v. sharply def., guard against Cd. 2837.

¹ The arc-line Pb 2657 is very weak but easily to be found in the spectrum of lead. It is situated exactly in the middle of the strong sharp line 2663 and the diffuse line 2651. The spark-line Pb⁺ 2562 is very intense when the self-induction is cut out.

² Before superimposing the substituted spectrum the dark-slide frame of the plate may be slightly shifted in the direction of the dispersion, whereby Sn 3656 may be made to move closer up to Pb 3684 and to stand out more clearly.

³ The first pair furnishes the sharpest coupling.

From Tables III–V already quoted the following intensity relations were found for the homologous pairs :

IN SPECIMEN No. I :

Sn.		Bi.		Hence
3009	>	3068	<	10% Bi.
3142	<	3068	>	0.2% Bi.
2765	<	2938	>	0.7% Bi.
3142	= (<)	2938	~ (<)	3% Bi.

Hence the proportion of bismuth, referred to the content of tin, was a little less than 3%, while referred to the basic substance lead, it was 0.03%.

IN SPECIMEN No. II :

Sn.		Bi.		Hence
3009	\gg	3068	\ll	10% Bi.
3142	\cong	3068	\sim	0.2%
2765	>	2938	<	0.7%
3142	>	2938	<	3%

Hence the proportion of bismuth, referred to the content of tin, was nearly 0.2%, while referred to the basic substance lead, it was 0.002%.

(f) THE APPLICATION OF THE RELATIVE OR CONCENTRATIONAL SENSITIVITY AS A MEANS OF ANALYSIS

The method of determining the concentrational or relative sensitivity of a spectrum-line and its theoretical significance in spectrum analysis was the subject of Chapter II. We shall now proceed to discuss the question whether, and in what way, the concentrational sensitivity of a spectrum-line is directly available for application in practical analysis. We shall show that it is possible with the aid of the known relative sensitivity of a line of an admixture A to devise a *wholly universal method* as a means of quantitatively analysing the proportion of A in any basic substance.

At the outset we wish to emphasize that it is generally impracticable to derive from the intensity relations of different spectrum-lines of an admixture conclusions respecting the concentration of A in the source of light (and hence in the substance of the electrode), or, still more generally, to infer the concentration x of A in P from the number of the spectrum-lines which are recognizable in the spectrum of a specimen $P + x\% A$. A. Reis, it is true, shows (cf. Chapter II, p. 27) that there are cases demonstrating the practicability of such an analysis in specific cases. Thus (fig. 38) it is a characteristic feature of a lead nitrate solution of 0.03% (by weight) that the “Pb-lines 3738 and 2662 are no longer discernible, whereas 2613, 3639, 4057 are still distinctly present,” or that “the Pb-concentration is less than 0.005% if the Pb-line 4057 only appears in the spectrum.” Quite apart from the fact that the

practical application of this method implies as a fundamental requirement that the whole of the electrical and photographic conditions, both in relation to energy and time, shall be strictly controllable and reproducible, and above all that the light transmitted by the spectrograph shall be of the same intensity throughout the whole range of wavelengths, the method is liable to lead to fundamentally false conclusions, as we have shown above. When discussing the absolute sensitivity we were able to demonstrate that the intensity ratio of two spectrum-lines of an element may be dependent upon the nature of another element present at the same time in the electrode, especially upon that of the primary substance.

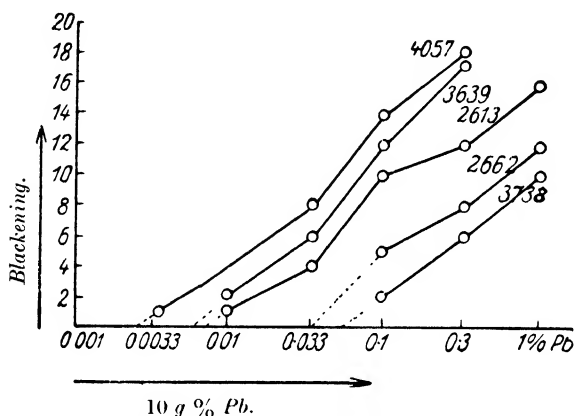


FIG. 38.—Concentrational sensitivity of different lines of lead in the solution spark.

In the case of lines of the same spectrum series and especially in that of different members of a multiplet, the order in which the lines vanish naturally persists under varying conditions of discharge and in all primary substances. Unless from causes discussed in Chapter II apparent discrepancies arise, the lines disappear in the inverse order of the physical intensities of the lines. Excellent examples in this connection are furnished by the triplets of cadmium and zinc, also by particularly striking groups of lines of scandium, of silicon, etc. Quantitative analysis by reference to the successive disappearance of these "physically like" lines of different intensities again implies, however, that all conditions under which the spectrograms are obtained may be strictly reproducible. There are nevertheless problems in analysis which are capable of being solved in this way. Such a case arises, for instance, where the ratio of the concentrations a , b , $c\%$ of cadmium in any primary substance causing the lines λ_1 , λ_2 , λ_3 of the triplets to vanish are known. If it be then required to determine the relative contents of cadmium in the given specimens, *e.g.* the progressive degree

of the removal of cadmium from a metal, the number of the cadmium lines which remain visible in the different specimens furnish a relative quantitative measure of the increasing degree of purity. As a matter of fact, even in these cases it is better to employ as the criterion of the "disappearance" of the lines, instead of the limit of detection or the actual vanishing point of the lines in their background, that point where the intensity of the line in question decreases to equality with that of a *very* faint neighbouring line of the primary substance. The procedure accordingly consists in comparing the specimens in which the cadmium lines λ_1 , λ_2 , λ_3 , successively become of the same intensity as the selected faint line λ_p of the primary substance. This procedure eliminates the influence of accidental variations in the blackness of the background (see fig. 37).

By the development of this method we arrive immediately at a *universal method* by which an admixture A in any primary substances P may be determined quantitatively without having to prepare for each primary substance standard alloys $P+a, b \dots \% A$. By way of illustration we will take the analysis of cadmium. For the quantitative determination of the element cadmium we employ by way of analysis-lines the first strong triplet of the I secondary series:¹

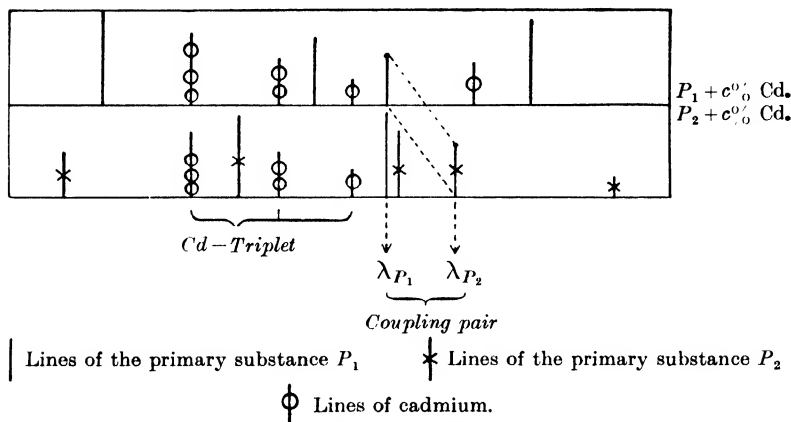
$$\left. \begin{array}{l} p_1 \quad d_3 \\ p_1 \quad d_2 \\ p_1 \quad d_1 \end{array} \right\} \begin{array}{l} 3615 \\ 3613 \\ 3611 \end{array} \quad \left. \begin{array}{l} p_2 \quad d_3 \\ p_2 \quad d_2 \end{array} \right\} \begin{array}{l} 3468 \\ 3466 \end{array} \quad p_3 \quad d_3 \quad 3404$$

The bracketed lines coincide in the authors' quartz spectrograph. Since now the intensity ratios of the individual components of the triplet are independent of the electrical conditions governing the discharge, while moreover the concentrational sensitivity of these lines is exactly the same, true relative intensities in the triplet are the same in all primary substances and at all concentrations. We are now able to place at our disposal the series of standard substances $P_1+a, b, c \dots \% \text{Cd}$ (*i.e.* the calibration scale), which can be prepared most conveniently. In addition, we shall have at hand a single chemically analysed specimen of the primary substance 2, *i.e.* $P_2+b\% \text{Cd}$. It will now be required to examine quantitatively a number of other specimens $P_2+x\% \text{Cd}$ with respect to cadmium. To this end the two spectra of $P_1+b\% \text{Cd}$ and $P_2+b\% \text{Cd}$ should by way of a preliminary experiment be photographed one below the other (fig. 39) in such a way that the triplet lines are of equal intensity in both spectra. A coupling of the spectra of the primary substance should now be established by searching out a line of P_1 and another of P_2 which are adjacent and of equal intensity.²

¹ We give the old simplified notation of the lines.

² This spectrographic coupling of the two spectra is much to be preferred to, *e.g.*, the insistence on exactly equal times of exposure, as the latter can never be reproduced with precision owing to variations in the spark discharge.

The spectra of the specimens $P_2 + x\%$ Cd which are to be analyzed should then be compared with those of the calibration scale $P_1 + a, b, c \dots \%$ Cd while maintaining the coupling of the primary substance. If we are able to find a coupled pair $\lambda_{P_1}, \lambda_{P_2}$ which is



The lengths of the lines indicate their intensities.

FIG. 39.

invariant within wide limits with respect to variations in the conditions of the electrical discharge we shall also be able to dispense with the chemically analyzed specimen $P_2 + b\%$ Cd when once this coupling pair has been ascertained.

The analytical procedure is then as follows: Spectra of the calibration scale $P_1 + a, b, c\%$ Cd and of the specimens under examination $P_2 + x\%$ Cd should be photographed on a plate one below another in such a way that the established lines of the coupling λ_{P_1} and λ_{P_2} are of equal intensity. (By preliminary trials the requisite time of exposure may be easily ascertained.) As the sparks are never exactly alike, uncertainty may be avoided by taking several spectrograms of the calibration scale and given specimens. These are then certain to contain pairs of P_1 and P_2 spectra with coupled lines λ_{P_1} and λ_{P_2} of equal intensity. In these the intensities of the Cd-lines should be compared. Equality of intensity of corresponding Cd-lines then signifies that the Cd-concentrations in P_1 and P_2 are alike.

We have further elaborated for this method a *table for the analysis of bismuth with respect to the presence of lead* based upon the use of the homologous pairs of Table I, p. 75, of *tin and lead* in $\text{Sn} + p\%$ Pb-alloys. From the spectra *a* and *b* shown diagrammatically in fig. 40 the invariant coupled pair of the Bi-line 4 and the Sn-line 8 was found when the time of exposure was such that the Pb-lines 1 and 7 or 5 and 10 respectively were of equal intensity in the Sn and Bi spectra. Let the

Pb-lines 10 and the Sn-line 9 now be supposed to constitute a homologous pair having its fixed point (*i.e.* equality of intensity) at 0.3% Pb in Sn (spectrum *d*). If now any Bi specimen whose spectrum (*c* in the diagram) is "correctly coupled" by equal intensities of 4 and 8 with the spectrum of Sn + 0.3% Pb be found to exhibit the same intensities of the Pb-lines as the latter (*d*), it would follow that this specimen of bismuth likewise contains 0.3% lead. All that is required therefore is to compare the intensity of the Pb-line 5 in the (Bi + $x\%$ Pb) spectrum with the intensity of the Sn-line 9 in the correctly coupled tin spectrum. By way of a coupling pair we found the spectrum-lines Sn 2780 and

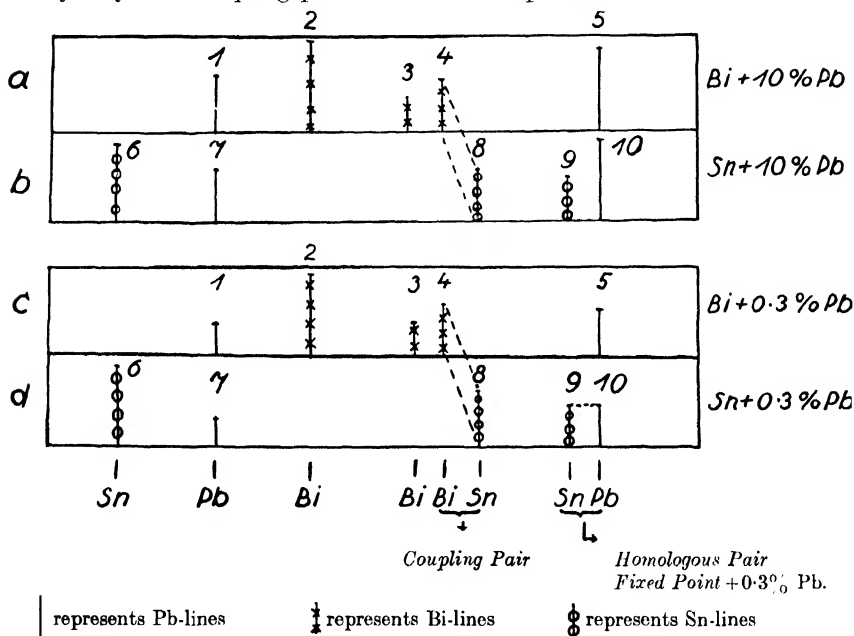


FIG. 40.

Bi 2597. To obtain correct coupling it was necessary to give approximately the same time of exposure in producing the spectra of Sn and Bi; while equality of intensity persisted also under varying conditions of discharge.

The procedure in the practical application of the analysis is as follows:

On a plate a few spectra of the specimen Bi + $x\%$ Pb and immediately below each of these a tin spectrum,¹ should be taken with approximately the same time of exposure. The pair of spectra in which the coupled lines Sn 2780, Bi 2697 are of equal intensity should then be sought and a homologous pair of lines established therein having its Pb-line in the

¹ It is of course quite immaterial as to whether the tin is pure or otherwise.

Bi-spectrum and the corresponding Sn-line in the Sn-spectrum of equal intensity. From the second column of the succeeding Table XII the proportion of lead present may then be found.

This analysis may then be still further refined by a simple modification. If the spectrum of tin be exposed about 8 times less than the Bi + $x\%$ Pb-spectrum so as to render the Bi-line 2516 and the Sn-line 2496 of equal intensity ("Coupled Pair II"), it is found that the same homologous pairs of the lead and tin-lines once more become equal in intensity when the lead concentration in the bismuth is 10 times smaller. The same homologous pairs which in the coupled pair I served for analysis between 10% and 0.01% of lead will now be available for analysis of specimens containing from 1 to 0.006% of lead.

In Table XII the first column reproduces the wavelengths of the comparison pairs, the second the fixed points for the analysis of Sn + $n\%$ Pb from the preceding Table I. The third column contains the fixed points of the pairs which are available for the analysis of lead in bismuth if the spectrum of the specimen be coupled with that of the tin by the coupling pair I noted at the head of the table. The fourth column contains a number of other fixed points which result if the other coupling pair II be taken for the two spectra. One thus obtains for each comparison pair a second fixed point which, as has been shown, lies roughly a tenth power lower than the first.

General significance attaches to the following fact which these experiments have established: The intensity coupling which was determined between the spectra of the primary substance P_1 and P_2 (*i.e.* in the instanced example, bismuth and tin) by the same admixture (*i.e.* lead) is wholly independent of the nature of the admixture. If spectrograms be taken of Bi + $a\%$ Pb and Sn + $a\%$ Pb while conforming to the intensity coupling by the Bi and Sn wavelength values given above, next if spectrograms be taken of Bi + $b\%$ Cd (or $c\%$ Zn) and Sn + $b\%$ Cd (or $c\%$ Zn, as the case may be), again conforming to the same intensity coupling, all cadmium or zinc lines will be of the same intensity in both spectra independently of the absolute value of b or c respectively. *Hence when once this coupled pair between two elements P_1 and P_2 is known and if tables of the homologous lines for P_2 with $A_1, A_2, A_3 \dots$ are available the proportions of these $A_1, A_2, A_3 \dots$ in P_1 may be determined quantitatively without recourse to any subsidiary investigation.*

The principle of the *equivalent relative sensitivity* of a spectrum-line of an admixture A in different primary substances provides the basis of a method for determining the amount of an impurity A in any primary substance. This may be shown by an example which was furnished in the course of one of our analyses. When establishing a calibration

TABLE XII

TABLE FOR THE ANALYSIS OF Pb IN Sn AND Bi

Coupling Pair I Bi = 2697 Å
 Sn = 2780 Å
 Coupling Pair II Bi = 2516 Å
 Sn = 2496 Å

} should be of equal intensity in pairs.

WAVELENGTHS OF THE LINES A	LINES OF EQUAL INTENSITY AT ATOMIC PER CENT. OF Pb GIVEN BELOW		
	for Pb in Sn	for Pb in Bi Coupling I	for Pb in Bi Coupling II
Pb=2833 Sn=2851	10 ¹	10	1
Pb=2663 Sn=2661	10 ²	10	1
Pb=2802 Sn=2851	3	Not amenable to observation since Pb coincides with a Bi-line.	
Pb=4058 Sn=3801	2		
Pb=2614 Sn=2594	1·3 ³	1·3	0·13
Pb=2823 Sn=2765	1·3 ⁴	1·3	0·13
Pb=2873 Sn=2765	0·6 ⁵	0·6	by extrapolation : 0·06
Pb=2802 Sn=2765	0·1	likewise not amenable to observation.	
Pb=2833 Sn=2765 ⁶	0·1	0·1	by extrapolation : 0·01
Pb=4058 Sn=3656	0·06	0·06	by extrapolation : 0·006

scale of Bi + *a*, *b*, *c*% Pb we were struck by the small concentrational sensitivity of the usually very sensitive lines of lead whenever the Pb-concentration fell below 0·1%. The lead contents of the specimens were known through their synthetical production, and repeated tests furnished confirmatory results. When passing on to lead contents of the order of 0·01% Pb the intensity of the lead-lines became independent of the concentration. From this it followed that the bismuth itself contained a proportion of lead which considerably exceeded 0·01%. We then proceeded to take spectrograms of Sn + 1% Pb and Bi + 1% Pb at exposures such that the whole of the lead-lines present became mutually alike in intensity. Next, a coupled pair of lines of tin and bismuth was sought whose equality was independent of the conditions

¹ to ⁵ cf. Table I.⁶ This pair was not specified in the original table.

of the discharge. Maintaining this coupling of the two spectra of the two primary spectra, we then proceeded to compare the spectrum of the "pure" bismuth in rotation with the spectra of Sn + 0.1% Pb, Sn + 0.03% Pb, Sn + 0.01% Pb. The lead-lines which were still present in our bismuth were now, on the one hand, more intense than the corresponding Pb-lines in (Sn + 0.03% Pb), on the other hand, they were weaker than those in (Sn + 0.1% Pb). By interpolation our Kahlbaum bismuth was found to contain 0.06% of lead.

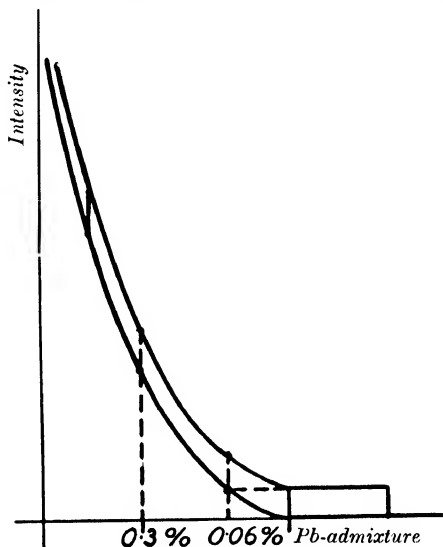


FIG. 41

Fig. 41 gives a graph of the intensity of a lead-line plotted as a function of the admixture of lead. The lower curve shows the decrease in the intensity corresponding to the true decrease of the lead content in the tin, the upper curve showing the decreasing intensity corresponding to the apparent decrease in the lead content in the bismuth. The differences in the ordinates then always furnish a measure of the intensity which the lead-line exhibits in "pure" bismuth. However, at a concentration of 0.3% already this ceases to be of importance, since in our calibration substance Bi + 0.3% Pb produced from the original bismuth the true lead content was 0.36%. It was therefore only 1.2 times greater than the apparent lead content, and cannot be distinguished with certainty from the apparent value by spectrum analysis, at least not without the assistance of a photometer.

(g) ANALYSIS BY MEANS OF THE RELATIVE SENSITIVITY

A further application of the quantitative method of analysis is furnished by the concentrational sensitivity when two spectrum-lines

of an admixture A have different relative sensitivities. This case arises, for instance, with the spectroscopically adjacent cadmium lines 2265 and 2313 Å. Both are lines of the cadmium ion Cd^+ , and both accordingly vary in like manner as the conditions of discharge vary. The concentrational sensitivity of 2265 is, however, much less than that of 2313 in that the former is the basic line of the principal series, *i.e.* an absorption line of the *ion*, whilst the latter is a line of a secondary series. The intensity ratio of these two lines differs accordingly with the different concentrations and is characteristic for the concentration. This intensity ratio is within wide limits independent of the conditions of discharge, hence also in like measure of the primary substance which contains the cadmium. We have not pursued these experiments any further. All the same it would appear practicable to develop this method into a very simple absolute analysis, *e.g.* by the application of any simple method of photometrically determining the intensity ratios of the two lines (cf. p. 108).

In this connection we should also like to mention the result of experiments which we have carried out upon the assumption of the *equal relative sensitivity of spectrum-lines of different substances* in consequence of our having frequently found this condition to obtain in our observations. Thus we had established that the intensity of the spectrum-line of an admixture A_1 varies with the concentration in a similar manner as the intensity of a spectrum-line of another admixture A_2 with the same change of concentration. We thus made an attempt to estimate the proportion of copper and silver in gold-copper and gold-silver alloys respectively, when the composition of only *one* of either alloy was known.

The variation in the intensity of the lead-lines as a function of the lead content (0.1% to 1%) in pure gold was determined by comparison with gold-lines, that is to say, we sought the gold-lines $\lambda_1, \lambda_2, \lambda_3$, which were of equal intensity with *one* of the lead-lines at $a, b, c\%$ lead. Next, in spectrograms of gold-silver, gold-copper and gold-copper-silver alloys with unknown Ag and Cu contents we associated in each a copper or a silver-line respectively with the *same* gold-lines $\lambda_1, \lambda_2, \lambda_3$, and from the ratio $a : b : c$ and an assumed unit Ag or Cu content of a specimen containing the smallest proportion of admixture, we proceeded to calculate the Ag and Cu contents respectively of the other specimens. The results are shown graphically in fig. 42, where the abscissae represent the true contents of copper (x) and silver (o) subsequently communicated to us and the ordinates the concentrations estimated by this procedure. It will be perceived that the estimated and true contents agree surprisingly well.

We do not suggest that this result is so general that equal relative

sensitivity may be assumed in *all* cases. Probably this is not the same in all cases, but there is little doubt that under fairly comparable conditions of excitation and with spectrum-lines of similar type the relative sensitivity furnishes an analytical means of rapidly establishing qualitative data respecting *concentrational ratios*.

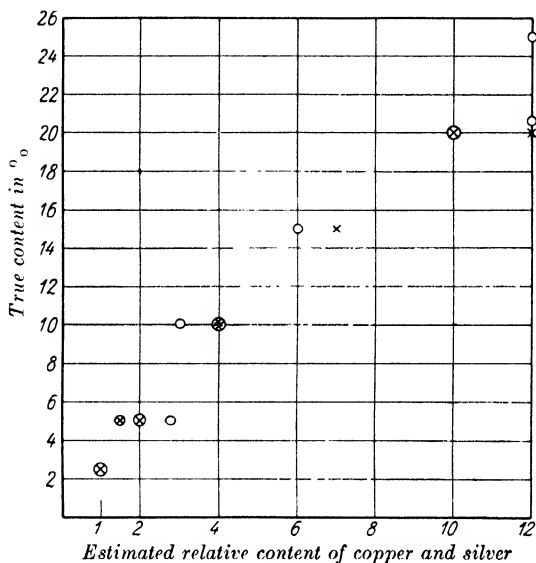


FIG. 42.

Finally, practical use may be made of the empirical fact that the visually estimated variation of the intensities of a spectrum-line of *A* corresponding to successive *A* contents advancing in powers of ten proceed approximately uniformly.

Estimates of this kind are of importance in the following instance. Let the variation of the intensity of a spectrum-line of an element *A* be known from spectrographic analyses, the element being present in any primary substance *P*, let us say, in proportions of 1% to 0.1%. Let it further be supposed that within the range of 0.1% to 0.01% a single alloy, *e.g.* one containing 0.01% *A*, is available. From the decrease in the intensity of lines between 1 and 0.1% it is then practicable to infer with a considerable degree of certainty the values of concentrations intermediate between 0.1% and 0.01%. A certain amount of experience is needed for this, which, however, is not difficult to acquire.¹ If, in addition, it be known in what manner the intensities of the lines to be

¹ We have initiated a considerable number of physicists in this method and have satisfied ourselves that this ability to arrive at correct estimates may be easily acquired.

estimated vary with the concentration when the element *A* is present in any other primary substance, it will be still easier to estimate the concentration.

In support of this we submit our investigations of the analysis of gold containing lead as impurity. We had at our command four standard specimens (I-IV) with lead contents of 0.96%, 0.19%, 0.026%, and 0.0035%. By the examination of (bismuth + *n*% lead) alloys we made ourselves conversant with the concentration-intensity relation. Next we proceeded to photograph the spectra of eight further specimens of gold debased by lead (*a-h*), ordered them into the series of standard specimens by comparing the lead-lines with the gold-lines, and then estimated the intermediate values. The result is recorded in the table appended below.

The first column records the notation of the specimen, the second the proportion of lead as ascertained by the above procedure, the third the percentage by chemical analysis, the fourth the ratio of the two values.

SPECIMEN	SPECTRUM ANALYSIS <i>S</i>	CHEMICAL ANALYSIS <i>C</i>	RATIO <i>C/S</i>
I	—	0.96	—
II	—	0.19	—
<i>d</i>	0.16	0.185	1.2
<i>a</i>	0.07	0.09	1.3
<i>h</i>	0.06	0.073	1.2
<i>c</i>	0.03	0.046	1.5
III	—	0.026	—
<i>c</i>	0.02	0.03	1.5
<i>g</i>	0.008	0.014	1.7
<i>b</i>	0.005	0.005	1.0
IV	—	0.0035	—
<i>f</i>	0.004	0.0027	0.7

We are now able to recognize a new significance in such measurements as have been made by A. Reis. The variations of the intensity of the spectrum-line of an element due to the variation of the concentration being known, unknown alloys may be analyzed with respect to this element *when a single alloy of the kind with a known content is available.*

CHAPTER VI

EXPERIMENTS ON THE REFINEMENT OF THE METHOD BY
PHOTOMETRIC INTENSITY MEASUREMENTS

We have already observed on p. 65 that an analysis based solely upon the photometric measurement of the intensity of the spectrum-lines of the substances which are to be identified qualitatively offers prospects of success in exceptional cases only.

The question, however, presented itself for investigation as to whether the "absolute" method described by us and the method of the substituted auxiliary spectrum are capable of being refined by photometric measurements. Two problems present themselves in this connection, viz. a more precise determination of the point of equality of intensity subsisting in homologous pairs or coupled pairs respectively, and the interpolation by instrumental measurement between two fixed points in the place of the visual mode of estimation.

(a) PHOTOMETRIC EVALUATION OF SPECTROGRAMS

It would take us much too far in an attempt to enter into the difficulties and pitfalls which generally abound in the process of evaluating spectrograms. We propose therefore to discuss those points only which arise in those cases where we were able to record a successful use of the photometric method of evaluation.

Photometric evaluation consists accordingly in determining the degree of blackening produced in the photographic plate by the lines of the spectrum, and in comparing the degree of blackening due to different lines of the spectrum, as for instance the two lines of a homologous pair of the primary substance and the admixture. Again we assume the condition to be satisfied that the spectrum-lines which are to be compared are situated within such regions of the spectrum with respect to which the photographic plate has like absolute and relative sensitivities; within which accordingly both the least amount of light necessary to effect a measurable degree of blackening and the gradation of the plate are the same throughout.

By "blackening" we may understand a relation subsisting between the light which is able to pass through the blackened portion of the plate and the intensity of the light which is allowed to fall upon the plate. It may also be regarded as a relation between the light trans-

mitted by the blackened strip and the light which is transmitted by the adjoining layer of the plate. We apply the latter relation, for it will be recalled that in the investigation in Chap. II (c) we found the limit of the practicable identification of a spectrum-line to be given by the point where it vanishes in the background of the emulsion. Since now the background, that is the degree of darkening of the portions of the plate adjoining the spectrum-lines, varies from point to point on the photographic plate it obviously becomes necessary to refer the measurement of the blackening of any line to the blackening of the immediately adjacent emulsion. Also, for the same reason it is necessary to make the surface element which is subjected to photometry smaller than the width of the spectrum-lines.

All photometers are fundamentally arranged upon the following basis (Diagram fig. 16, in Chapter III): A diminished image of a slit Sp illuminated by a source of light L through a lens L_1 is formed by means of a microscope lens combination L_2 upon the photographic plate; the brightness of this illuminated surface is determined from the other side by some photometric method. By displacement of the plate P spectrum-lines or the adjacent background can be photometrically measured.

The diminished image of the slit will then be either wider or narrower than the line which is to be measured photometrically. The case where both are of equal width may be ignored, since the width of different lines of the spectrum is not equal. For the same reason a slit image which is wider than the spectrum-line may be left out of consideration; for in such a case the photometer would furnish entirely different results from those obtained by visual comparison by means of a magnifier, as will readily be gathered from the following consideration. Of the surface F of the slit image on the plate let the portion f' be occupied by the spectrum-line λ' and f'' by λ'' respectively. Let I be the intensity of the light which is transmitted through unit area of the background (which we will suppose to be alike about λ' and λ''), and let i' , i'' be respectively the intensity of the light transmitted through unit area of the blackened line surfaces for λ' , λ'' .

The degree of blackening, as judged by the eye, will then be equal when

$$i' = i''.$$

The photometer, on the other hand, establishes equality when the quantities of light transmitted through the slit-image as a whole are alike, *i.e.* when

$$(F - f') I + f' i' = (F - f'') I + f'' i'',$$

i.e. when

$$f' (I - i') = f'' (I - i'').$$

It is only when $f' = f''$, *i.e.* when the widths of the spectrum-lines are exactly equal, that the photometer will show equality for $i' = i''$.

Lastly, the width of the photometer slit may be less than the width of the line. The distribution of the intensity within the spectrum-line should be measured, which will show the place of greatest density. This mode of photometric comparison will likewise differ from the visual estimation with the aid of the magnifying lens, since the latter, owing to its deficient resolving power, will in all cases furnish a mean value only. Thus, where the photometer furnishes for the distribution of the photographic density in two spectrum-lines the curves *a* and *b* (fig. 43) the eye will in most cases judge *b* to be more intense than *a*.

From this example it will be seen that there are objections to the photometric refinement of visual estimations. It would be practicable, of course, to employ the last mentioned mode of measurement of the distribution of the intensity and to refer the whole of the analyses to these measurements.

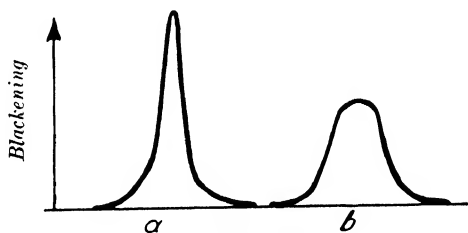


FIG. 43.

In that case, however, the analytical table would be applicable only to spectrum apparatus having one particular and invariable width of slit since the true (physical) form of the spectrum-lines is always modified by the width of the slit and the dispersion of the spectrum apparatus used.

There is, however, one case in which the photometric measurement takes us distinctly further than the visual estimation. Where, within the region of the spectrum which contains the lines used for the analysis, the dispersion is such that even with a wide slit no spectrum-lines appear masked the spectrograms may be taken with a slit the width of which is always considerably greater than the true width of the lines.

The plate will then exhibit in the place of the "lines" blackened "surfaces," the photographic density of which is perfectly homogeneous when the apparatus is correctly adjusted.

The photometer slit should now be set to such a width that its image may lie within the uniformly blackened "spectrum surface." The greater this width, the easier is the measurement. It may be carried

out with adequate precision with any simple model of the Hartmann photometer.

We have made a number of observations in individual cases to ascertain to what extent the photometric mode of measurement thus applied could be made to increase the accuracy of the result. Alloys of tin and cadmium were prepared having closely graded concentrations. It was found possible, to give an instance, to distinguish three grades of concentrations situated between 0.6% and 0.7% cadmium. The results were reproducible within $\pm 2.5\%$. In the analysis of platinum, with respect to rhodium and iridium we were able to record between 5% and 0.5% a degree of photometric accuracy of $\pm 5\%$. It is inferior to that attained in the previously instanced case owing to the fact, in the first place, that the lines are so closely adjacent that the slit cannot be made very wide, and, secondly, the spectrograms are apparently not reproducible to the same degree as is the case with metals having a higher vapour density.

(b) THE LOGARITHMIC WEDGE SECTOR METHOD OF PHOTOMETRIC SPECTRUM ANALYSIS.

An entirely different method of photometrically refining the chemical spectrum analysis has been adopted by G. Scheibe,¹ using the logarithmic sector method according to Hamburger and Holst. In his method the provision for photometric measurement is already allocated to the earlier stage of taking the spectrogram. While ordinarily it is a fundamental condition when photographing a spectrum for analytical purposes that the slit of the spectrogram should be uniformly illuminated throughout, as far as practicable, in the new method the intensity of illumination is varied intentionally and systematically from point to point along the slit. Since a prism spectrograph produces a stigmatic image of the slit,—in that each element of the slit has corresponding to it an element of the spectrum-line on the plate,—it follows that the photographic blackening of the spectrum-lines along its length will exhibit the same variations as the intensity of illumination within the slit. The best means, according to Hamburger and Holst, of obtaining such a uniform variation of the illumination along the slit is afforded by a rotating sector set up in front of the slit. In fig. 44 the slit of the spectrograph is indicated by the broad black bar. Between the slit and the source of light there is an opaque disc *D* which revolves about its centre *C* and is provided with an aperture *E*. If the slit be uniformly illuminated by the source of light it follows that as the sector rotates about *C* the upper portion of the slit will receive the shortest and the lower portion the most prolonged radiation quite

¹ G. SCHEIBE and NEURÄUSSER, *Z. angew. Chem.* 41. (1928), 1218.

independently of the rate of rotation. Hence through the successive portions of the slit a continuously varying quantity of light will be transmitted, with the result that the spectrum-line will appear on the plate most densely blackened at one end and least so at the other end. Given a choice of appropriate times of exposure two spectrum-lines of different intensities will accordingly be of different lengths, since the

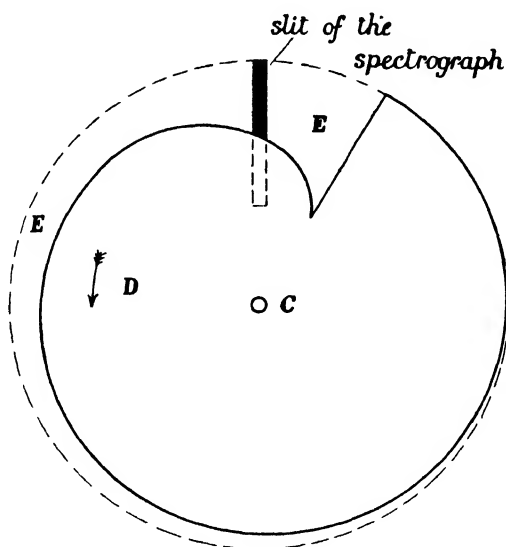


FIG. 44.

fainter spectrum-line, even under prolonged exposure, does not give enough light to the plate to blacken it throughout the same length as the stronger line. The spectrum of a source of light having its radiation passed through the sector has accordingly the appearance indicated in fig. 45. Since now the photographic density curve of a plate is nearly



FIG. 45.

a logarithmic function of the amount of light, the sector is appropriately given such a form that the time of exposure may likewise vary logarithmically from point to point of the slit. *The difference of the lengths of two lines in the spectrogram will then be approximately pro-*

portional to the logarithm of the ratio of the intensities of these lines.¹ The application of this method demands an exceedingly well made spectrograph slit, which when made extremely narrow also requires to be perfectly free from defects (such as dust and jagged edges).

As a means of ensuring the absolutely requisite degree of uniform illumination of the rotating sector Twyman and Simeon² recommend the following arrangement (Fig. 46). The rays proceeding from the source of light F are rendered parallel by the lens L_1 . The rotating

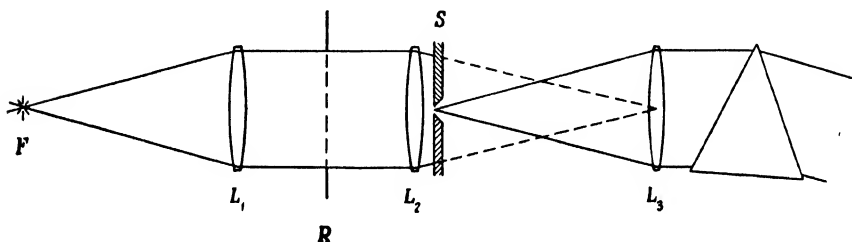


FIG. 46.

sector is placed in the region of the parallel rays. By a second lens L_2 placed immediately in front of the slit S of the spectrograph these parallel rays are rendered convergent so as to produce a sharp image of F on the collimator lens L_3 of the spectrograph.

Since Scheibe's deduction is open to question³ it will not be out of place to outline the theory of the method. It is assumed that the law

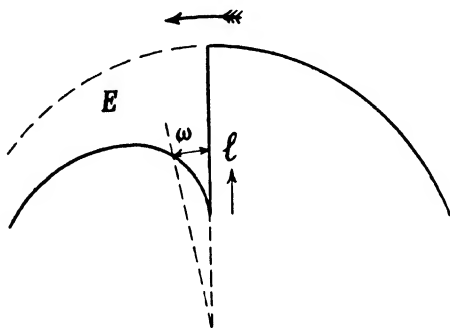


FIG. 47.

of Schwarzschild holds good, that is, that the blackening of the photographic plate is governed by the product It^p (p being Schwarzschild's constant) and that the blackening S is proportional to $\log I$.

It is required to determine the intensity relation $I_1:I_2$ of two spectrum-lines. If the spectrum be photographed through the rotating

¹ Twyman and Simeon. *Trans. Opt. Soc.*, 31, 169-183, 1929-30.

² *Loc. cit.*

³ This was subsequently also pointed out by Scheibe himself.

sector the time t during which every point of the spectrum line receives light will be proportional to the opening ω of the rotating sector at that point. Now, the opening of the sector should be so formed that the logarithm of its opening may be proportional to the distance of the point from the zero point of the sector (Fig. 47), *i.e.*

$$\log \omega = \beta \times l \text{ (where } \beta \text{ is a constant).}$$

Since according to Schwarzschild's law two spectrum lines present equal blackening when

$$\frac{I_1}{I_2} = \left(\frac{t_2}{t_1} \right)^p,$$

where t_1, t_2 are the times of exposure, we obtain as the condition of *equality of blackening* when photographing through the sector :

$$\frac{I_1}{I_2} = \left(\frac{\omega_2}{\omega_1} \right)^p,$$

or
$$\log \frac{I_1}{I_2} = \beta p (l_2 - l_1) = \beta' p (L_2 - L_1),$$

the difference in length of line δL being measured from any convenient horizontal datum in the spectrum.

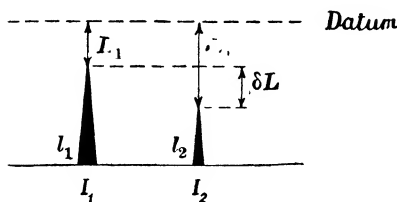


FIG. 48.

The method is particularly well adapted for accurately establishing the fixation points of the homologous pairs of lines, that is for ascertaining equal intensities. It likewise furnishes analyses of concentration.

For example, let a spectrum of $P + a\%A$ and a spectrum of $P + b\%A$ be photographed through the rotating sector (a and b being low concentrations). Let the intensity of a spectrum-line of the primary substance P be I_1 , that of a line of the admixture A being I_2 (at $a\%$) and I'_2 (at $b\%$). Then from the difference of the lengths of these spectrum-lines in the two spectrograms we find directly

$$\log \frac{I_1}{I_2} \times \frac{I'_2}{I_1} = \beta' p (\delta L - \delta L') = \log \frac{b}{a},$$

that is to say, the ratio of the concentrations. Where an alloy $P + a\%A$ is known it will be practicable to ascertain other concentrations $b\%, c\% \dots$.

CHAPTER VII

SPECIAL PROBLEMS : " LOCAL ANALYSIS "

The very essence of the spectro-analytical method is put to full account in the problem of " local analysis." By this we understand the method of ascertaining the composition of any locally restricted portion of a substance. The solution of this problem is practicable by the spectrographic method, thanks to the extremely small amount of material required for the analysis, and the possibility of confining the spark discharge strictly to one spot.

(a) A FEW EXAMPLES FROM ACTUAL PRACTICE

We have repeatedly carried out analyses of this kind where every other method had proved abortive. Thus, on one occasion we received a fragment of a gold alloy which exhibited small whitish specks distinctly enough to be seen through a magnifying glass. A spectrogram obtained from a spark discharge between such a speck and a fine electrode of purest gold set directly opposite to it disclosed the presence of inclusions of palladium. On other occasions specks appearing upon finished articles could be shown to be mercury, tin, and iron, while minute granular specks embedded in a piece of metal were shown to be particles of the crucible.

On several occasions we were called upon to examine *rolled or pressed pieces* at the places where they had cracked. Whereas the metallographic examination only sufficed to demonstrate the presence of dissimilarities in the microstructure, the spectrographic analysis disclosed in one case that the cracked portion of an alloy contained an excess of zinc. In another case where finished pressed articles had shown cracks after prolonged storage it could be shown beyond doubt that the inner sides of the finely jagged fractures contained large proportions of barium and strontium, though neither element was found to be present at the surface of the cracks or in that of *sections cut* from the material. On being bent, the sheet showed fresh fractures which again invariably disclosed the presence of barium and strontium. From this it was reasonable to infer that the cracks were already present (produced at the time when the material was being operated upon with a polishing medium containing barium and strontium), and that they widened subsequently during storage.

In another case a test was to be applied to ascertain whether a very thin fragment of sheet metal consisted *throughout its entire thickness of uniformly pure precious metal*. After repeated spectrographic tests applied to the same spot and "sparking off" after each application it could be shown that the surface layer contained pure precious metal, but that under the surface the metal was alloyed.

A special case of local analysis arises when the degree of *uniform purity* or the uniformity of the composition of a casting, for example, is to be ascertained. As in these cases the examination is of a purely comparative kind, the test being mostly made in continuous rotation, this test is both simple and exact. Again only minute quantities of the material are needed. These may be cut from various parts of the casting and even when many specimens are taken the loss of material is negligibly small.

In this connection reference may be made once again to the frequently abnormal distribution of iron, as mentioned on p. 64.

As regards tests applied to ascertain the *quantitative* uniformity of the composition of an alloy at all points, we may here refer to the general statements respecting the attainable degrees of accuracy which have already been made. When it is required to ascertain whether the degree of purity is equally good at all points the direct *method of comparison* (Chapter V, *b*) is particularly effective, all the more so since this is a test which altogether exceeds the resources of chemical analysis, whilst it can be applied with the utmost ease and great precision through the medium of spectrographic analysis. We have carried out experiments of this kind on several occasions, for instance, by way of verifying the chemical purity of platinum castings and the uniformity of the distribution of the components of alloys. In many cases regions were found where the purity was below standard. The impurities in these cases were so slight that, were the whole block used up in the analysis, it would have been impracticable to determine the presence of the impurity by chemical analysis.

A further application of the method consists in the investigation of the phenomenon of segregation, the establishment of which is also desirable in metallographic investigations of a purely scientific order.

Another problem which presents itself is the investigation of the process of refinement of metals. The object of this process is to induce the elimination of minute quantities of the other phase, the latter being of such a kind that its direct metallographic identification has not yet been successfully accomplished. It would seem that this may be achieved with the aid of spectrum analysis. At any rate it is practicable by its means to ascertain whether the purity of the individual specimens is uniform in degree, which obviates thermal refining effects

being simulated by accidental impurities. Chemical analysis is not applicable in these cases in view of the smallness of the available samples and the minuteness of the likely impurities. Finally, it is an undoubted advantage to be able to apply the analysis to a specimen and then with the *same specimen* to apply all necessary mechanical and electrical tests. In this way the spectrographic method of analysis bids fair to become a new medium of metallographic investigation.

As further instances of the application of the spectrographic method of local analysis we may mention experiments made to prove by the spectroscopic method the correctness of Tammann's limits of resistance to the action of nitric acid. Alloys of purest gold with silver, with copper, and with silver and copper were examined spectro-analytically and the intensity of the silver- and copper-lines relatively to the gold-lines determined before and after boiling in fresh concentrated nitric acid. The alloys contained :

Specimen No. I	-	-	2.5% Ag	2.5% Cu
Specimen No. II	-	-	20 % Ag	5 % Cu
Specimen No. III	-	-	1% Ag	25 % Cu

Specimen No. III has accordingly approximately as many Cu atoms as it has Au atoms. It was found that in all these alloys boiling in nitric acid exercised no influence upon the silver and copper content, so that the protective action of gold found by Tammann obtains also in the uppermost layers of the alloys.

Experiments in which the same method is employed to ascertain coefficients of diffusion of metals are now proceeding.

(b) THE GRAIN BOUNDARY EFFECT

As a specially interesting case of the application of local analyses, we may mention the spectrographically adduced proof that impurities of lead in gold are deposited in the major part at the grain boundary and thereby give rise to the brittleness of gold containing lead. When, for instance, a specimen of gold containing 1% of lead was fractured the content of lead in the first spectrogram taken from the fresh fracture was invariably many times greater than that obtained from a cut specimen. Very short exposures of a few seconds taken from fresh fractures exhibited even an *excess of lead over the gold*. When now a more extensive series of spectrograms was photographed the intensity of the lead-lines diminished and finally became constant (figs. 49, 50, 51). The constant amount was, however, exactly the same as that exhibited by the cut specimen. The difference between a fractured and a cut electrode became less pronounced with decreasing contents of lead, which is in keeping with the smaller decrease in the intensity. When the lead content is only a few hundredths per cent. the difference vanishes.

The subjoined fig. 49 shows spectrograms derived from such an experiment, which was made with an Au + 0.8% Pb. alloy. It shows the decrease of the intensity of the lead-lines in the successive spectra. The first spectrum was derived from a fresh fracture given an exposure of 10 seconds. The succeeding spectra are shown in the spectrograms which were taken next, the exposure in each case being ten seconds.

We have made a few further experiments with the fractured (Gold + $n\%$ lead) specimens, one of which we should like to refer to at this place. Such a fracture of the Au + 1% Pb specimen with a high lead content which had not been sparked was etched with hot concentrated nitric acid. Under this treatment the lead content in the first spark discharge had become very small, and there was only a just recognizable decline in the next spectrogram, after which the point of constancy



FIG. 49.—Fracture
Gold + 0.8% Lead.

Decrease in the intensity of lead-lines compared with those of gold, in successive spectrograms.

appeared. But now the constant value of the lead intensity was such as might indicate that there was 30% less lead in the gold (*i.e.* only 0.7%). It is obvious from this experiment that the nitric acid had more deeply lixiviated the lead, so that a considerable layer of the electrode surface had to be volatilized in the spark discharge before the normal mean value was restored. Specimens of gold containing 0.2% of lead still show a marked difference between fractured and cut specimens. By etching with nitric acid the great initial intensity of the lead-lines vanishes likewise with this concentration, and the constant final value appears only after the third or fourth 10-second exposure, which, as a matter of fact, is then also attained by the unetched specimens. At 0.2% the grain boundaries are already so narrow that the nitric acid

only attacks the more or less exposed ones, but is unable to penetrate between the grains.

The subjoined diagram (fig. 50) gives quantitative data of the decrease of the intensity of the lines of lead, *i.e.* the apparent lead contents derived from successive spectrograms 1, 2, 3, etc. In the diagram the curve represented by solid lines shows the mean lead content of a fresh fracture. The first 10-seconds spectrogram shows an estimated Pb content of 40%, while the mean lead content is only 1%. The cut specimen shows initially about 6%, *i.e.* considerably less than the fracture. The specimen etched with HNO_3 (interrupted line curve) gives for the 1% specimen a permanently lower value, not so for the 0.2% specimen. In the succeeding table the figures under the head of "apparent lead content" signify the amount of lead which would be

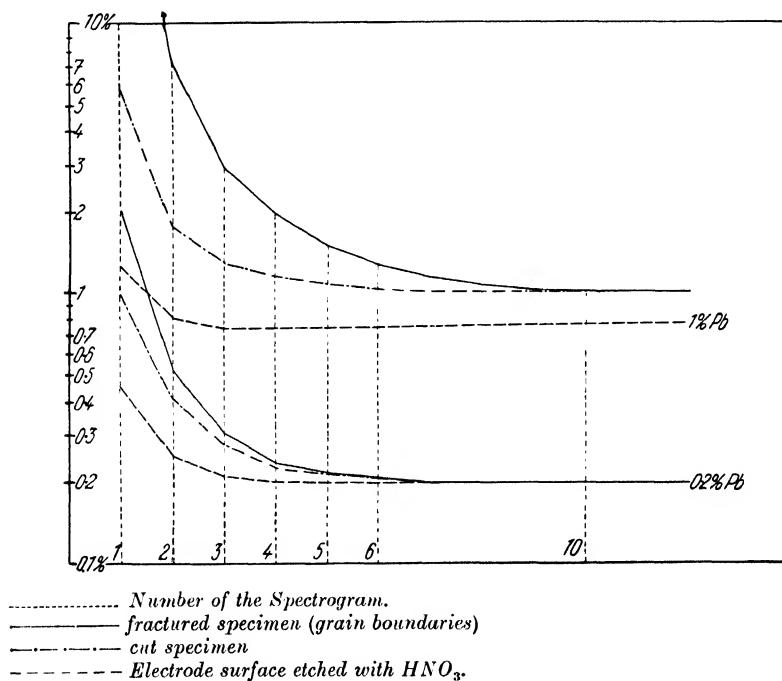


FIG. 50.

inferred from the intensity of the lines of lead relatively to those of the gold-lines in successive spectrograms.

It does not seem superfluous to furnish a proof that the analysis of the gold-lead specimens yields true values at the grain boundaries despite this accumulation of the lead (in the form of a gold-lead compound). The fact, referred to above, to the effect that the intensities of the lines of lead remain entirely constant (fig. 51) after the

phenomenon of the decreasing intensity has ceased, even during very prolonged sparking, shows that the spark discharges give rise during the exposure to an average uniform volatilization of the internal regions of the crystals and grain boundaries. We have, however, carried out a set of special experiments regarding the intensities of the lines of lead, in one case with lead in *gold*, in another with lead in *tin*. *Tin + n% lead did not exhibit this phenomenon of the decrease in the intensity.*

SPECTRO- GRAM No.	TRUE Pb CONTENT 1% APPARENT Pb CONTENT			TRUE Pb CONTENT 0.2% APPARENT Pb CONTENT		
	Fractured Specimen	Cut Specimen	Etched Specimen	Fractured Specimen	Cut Specimen	Etched Specimen
1	40	5-6	1	2	1	0.45
2	7	2	0.8	0.5	0.42	0.25
3	3	1.2	0.7	0.32	0.28	—
4	2	—	—	—	—	0.2
5	1.5	—	—	—	—	—
6	—	1	—	—	—	—
7	—	—	—	0.2	0.2	—
10	1	1	0.7	0.2	0.2	0.2
•	1	1	1	0.2	0.2	0.2

A spectrogram was taken of a sample of Au + 1% Pb and under it a spectrum of Sn + 1% Pb. Since gold has a very small vapour pressure relatively to tin the spectrum of the latter is considerably more intense than that of gold. The times of exposure were then so varied that a line of lead in the spectrum of Au + 1% Pb acquired exactly the same intensity as the same line in the spectrum of Sn + 1% Pb.¹ Next, the spectra of other specimens, *i.e.* Au + 0.1% Pb and Sn + 0.1% Pb, Au + 0.01% Pb and Sn + 0.01% Pb, were photographed, so that the intensity relations between the lines of primary substances Au and Sn remained exactly the same as those obtaining in the correctly coupled 1% Pb spectra. In practice ² this is accomplished by reproducing the condition of equality of intensity of a coupled pair made up of an Sn-line and an Au-line. The selected line of lead in the gold and tin spectra will continue to exhibit the same intensity. Experiments made upon other lines of Pb have verified this result. This shows therefore that for the spark discharge between electrodes made up of Au + *n*% Pb, after sparking off the exposed grain boundaries, the lead behaves exactly as though it were distributed therein as uniformly as in the tin.

¹ To obtain correct coupling the ratio of the times of exposure was about 60 : 1.

² cf. Chap. III, *e, f, g*, where methods of such investigations are discussed in detail,

These experiments demonstrated yet a further fact in metallographic chemistry. When the specimens of gold contained a little copper in addition to lead, approximately of the order of quantity of the lead content, the *copper was found to exhibit precisely the same grain boundary effect as the lead* (fig. 52). *Gold-copper without lead, on the other hand, showed a permanently constant copper-line intensity.* From this it may be inferred that the copper and the lead are structurally arranged in the same manner. The brittle grain boundary layer is accordingly either an Au-Pb, or a Pb-Cu compound. If silver happened to be present as well the intensity of the Ag-spectrum-lines

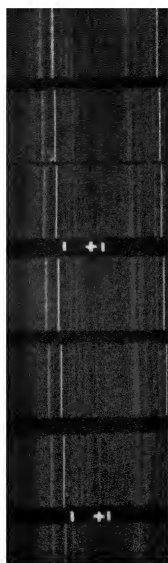


FIG. 51.—Constancy of the intensities of the lines of lead (+) relatively to the gold-lines (|). Spectrograms obtained after prolonged sparking off of the grain boundaries.

was found to remain constant, which showed that the silver was evenly distributed in the gold (see fig. 52). Etching experiments with nitric acid showed moreover that the copper vanished with the lead, not so the silver; whereas in lead-free alloys the copper, like the silver, showed itself to be completely protected by the gold (see above).

To the interpretation of the above experiments in terms of grain boundary effect, *i.e.* as experimental evidence for the assumption that the lead occurs between the crystalline granules of the gold, it might be objected that in the course of the unavoidable heating of the electrode surface, lead volatilizes more rapidly by reason of its high vapour pressure than the gold, much in the same way as it is practi-

cable by heating brass *in vacuo* to distil out the constituent zinc. There are, however, a number of experimental data which disarm this objection. In the first place we have in this connection the above-mentioned experiments demonstrating the equal relative sensitivity of the lines of lead in gold and tin. Next, there is no intelligible reason why specimens containing lead to the extent of 0.1% upwards should behave differently from those of lower concentrations, since all specimens are examined in precisely the same manner. What supports our

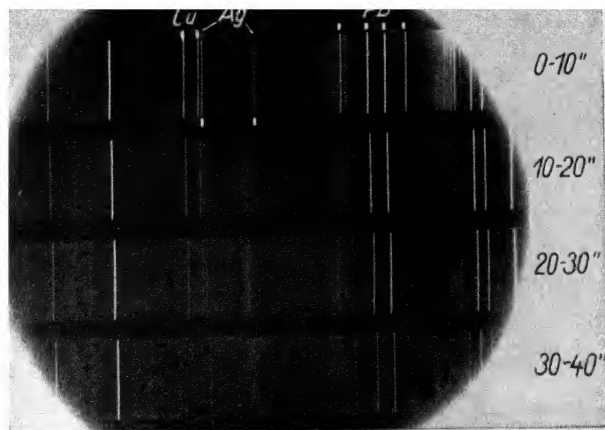


FIG. 52.—Fracture of gold + 1% lead.

1. Exposures 0—10 secs.
2. Exposures 10—20 secs.
3. Exposures 20—30 secs.
4. Exposures 30—40 secs.

The spectrograms clearly show the decrease of the intensity of the lead-lines, as well as of the copper-lines, whereas that of the silver-lines does not show any decrease. The somewhat greater intensity of the silver-lines in the first spectrogram as compared with the succeeding ones is due to the slightly more intense exposure in the former.

interpretation more forcibly than any other argument is the fact that the copper in gold containing lead behaves exactly as does the lead. Finally, analyses of tin contaminated with a small proportion of mercury do not show this effect, although in this case similar differences in the vapour pressures of the primary substance and the secondary substance are present. It is only when the heating is carried so far that thermal loosening results, and ultimately fusion of the crystalline lattice, that the freely volatile element passes before the other into the spark-gap so as to produce a more intense effect in the spectrogram than conforms to the true mean content of the alloy. This, in fact, is the basis of the method described on p. 60 for demonstrating the pre-

sence of minute quantities of elements of a high vapour pressure in primary substances of a low vapour pressure.

Finally, the experiments of L. Nowack¹ provide a direct metallographic proof that within the range of concentration, in which the grain boundary effect was observed by us spectroscopically, the lead actually does lie in the grain boundaries. The photo-micrograph of a polished metal section² (fig. 53) by L. Nowack was taken from an alloy of gold containing 0.06% Pb. It shows clearly the segregation of the gold-lead compound Au_2Pb in the grain boundaries.

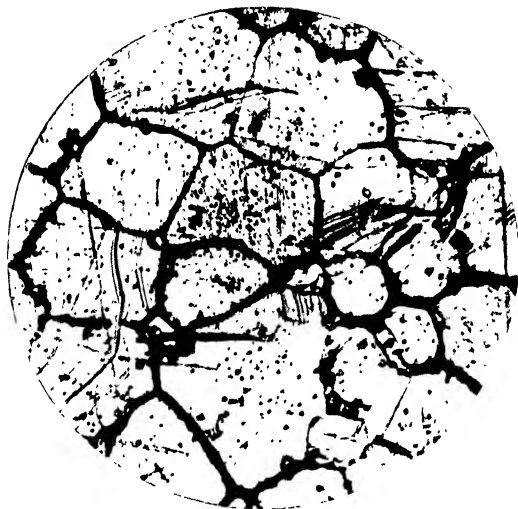


FIG. 53.

(c) FUNDAMENTAL SIGNIFICANCE OF LOCAL ANALYSIS IN RELATION TO THE INTERPRETATION OF SPECTRO-ANALYTICAL DATA

It may now be useful to discuss a little more fully the specific nature of the spectro-analytical method as such, in comparison with chemical analysis. We were able to show by a practical example furnished by our experiments that the chemical analysis can only disclose the mean purity of a specimen, so that a specimen may appear to contain a constitutional impurity *A* when in reality *A* may only be present as an accidental local inclusion.

A similar false inference may, however, also be derived from the spectro-analytical method. Take the case of the analysis of a casting. In such a casting it may happen in consequence of two factors in particular that different portions of it differ in their composition. In

¹ L. NOWACK, *Z. anorg. u. allg. Chem.* 154 (1926), 395.


² The illustration, which L. NOWACK has kindly provided, represents an unetched section of a sample annealed for a long time at 650°.

the first place segregation may occur, that is, the constituents of the alloy may have separated. Secondly, in general, the crystals in the marginal zone are much larger than within, so that here the grain boundaries or the surfaces of the crystals will be larger than at the outer zone. Impurities which become deposited at the grain boundaries will therefore be more concentrated within the casting than in the outer zone.

A casting is usually analysed chemically by drilling out various portions of the surface layers and the interior, mixing the drillings, and then applying the chemical tests. Any separation of the constituents which may have occurred in the casting naturally remains unobserved just as does the distribution of the impurities. On the other hand, the chemical analysis shows the mean impurity of the material. The spectro-analytical method shows both the distribution of the constituents of an alloy and the degree of purity at the drilled places, but it fails in supplying reliable indications of the mean degree of impurity.

Either method supplies accordingly *certain* data, but these are *not of the same nature*. This should not be left out of sight, and, when deciding upon one or the other method or when interpreting and drawing inferences from data respecting the "purity" of a sample this should be carefully taken into consideration. Where a casting is subsequently to be remelted in smaller ingots the chemical analysis will supply the required information (assuming that the question of segregation or the distribution of *A* does not enter into consideration). Where, on the other hand, an ingot is cut into portions which in their turn are re-cast or rolled or drawn the required data will be furnished by the spectro-analytical examination of the various portions. Where the block is rolled or drawn neither the chemical nor the spectro-analytical method will furnish conclusive data. Where drillings from various zones of the block have been examined by spectrum analysis it will be practicable to state the maximum proportion of impurity in the material. Where the mixed drilled chips have been analysed chemically it will be practicable only to state the mean degree of purity, but allowance must be made for the probable existence of zones of sheets or wires containing a greater or smaller percentage of impurities.

Where accordingly it is a matter of being quite certain regarding the purity of a material, such as that of a platinum wire for use in a resistance thermometer of high precision, there is no other way of securing this degree of certainty but by examining fragment after fragment of the wire. This can only be done with the aid of the spectrographic method, both by reason of the small amounts of wire needed and the rapidity with which the test can be applied.



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